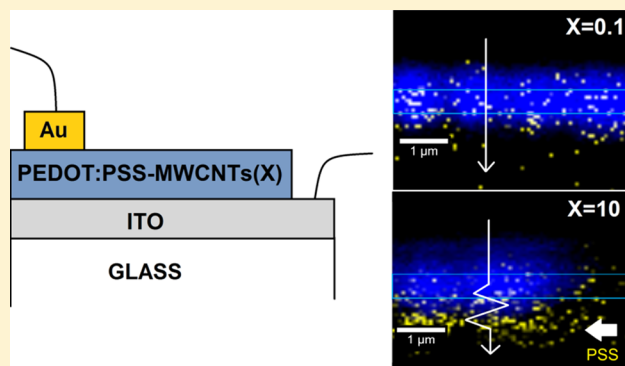


Raman Microscopy Insights on the Out-of-Plane Electrical Transport of Carbon Nanotube-Doped PEDOT:PSS Electrodes for Solar Cell Applications

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ABSTRACT: In the present report, we focused on the study of the out-of-plane electrical transport of multiwalled carbon nanotube (MWCNT)-doped poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) composites (PEDOT:PSS-MWCNTs(X)) as electrodes for solar cell applications. The out-of-plane direct current and alternating current electrical transport, rarely studied but not less relevant, was additionally supported with in-plane and out-of-plane confocal Raman microscopy and grazing incidence small-angle X-ray scattering characterizations. The main relevance of our study is the monitoring of the polymer structure all across the polymeric film by using confocal Raman spectroscopy and its correlation with electrical transport. Modifications in the PEDOT benzenoid and quinoid conformations were observed in the vicinities of MWCNTs, and the enrichment of PSS at the indium tin oxide electrode interface was also evidenced. In consequence, the low MWCNT loadings into PEDOT:PSS lead to an increase of the out-of-plane conductivity, but the heavier MWCNT loadings lead to a drastic decrease. The tuning of the doping level of these polymer composites and the understanding of the interface structure are crucial to fabricate electrodes with higher out-of-plane conductivities for organic solar cell applications.



1. INTRODUCTION

Conductive polymeric nanocomposites have attracted recent interest in the scientific community due to their outstanding properties for energy storage¹ and conversion² applications. In the particular case of hybrid solar cells, conductive polymer nanocomposites are being studied as either promising active layers^{3,4} or electrode countermaterials.^{5,6} The conductive poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)-doped polymer is one of the most used as transparent electrodes in organic and hybrid solar cells.^{7–9} The deposition of PEDOT:PSS over an indium tin oxide (ITO) layer has shown an improvement in the stabilization of its work function, in the overall planarization of the films,^{8–10} and in the smoothing of the electrode interface contacts.¹¹ In the last few years, the majority of the PEDOT:PSS electrode studies have been focused on in-plane electrical transport characterization showing electrical conductivities up to $\sim 10^3$ S cm⁻¹. However, the use of PEDOT:PSS and its composites as electrodes for solar cells and other devices requires a better understanding of the out-of-plane electrical transport, which is still rarely reported.^{11–16} The out-of-plane conductivity of PEDOT:PSS has shown a large anisotropy showing a decrease of several orders of magnitude (10^{-6} – 10^{-4} S cm⁻¹) with respect to the in-plane conductivity, depending on the formulations.^{11–16} Previous structural insights for PEDOT:PSS

films using scanning electron microscopy, atomic force microscopy (AFM), and scanning tunneling microscopy techniques have already revealed that the segregation of PSS could lead to drastic consequences on the electrical transport.^{17–19} In addition, there have been recent reports showing efforts to enhance the PEDOT:PSS conductivity by the addition of small amounts of carbon nanographite²⁰ and nanotubes^{21–25} as secondary dopants, leading to an increase in the in-plane conductivity of about three times. However, there are no studies focusing on the effect of multiwalled carbon nanotubes (MWCNTs), which are metallic in nature, on the structural characteristics, especially at the interface with the ITO layer, and their consequences on the out-of-plane conductivity of MWCNT-doped PEDOT:PSS films. In this report, besides a complete characterization of the film structures, we aim to show, for the first time, in-plane and out-of-plane profile confocal Raman microscopy characterizations of these electrodes. Our main contribution is the monitoring of different polymer conformations across the films by using confocal Raman microscopy and its correlations with

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the out-of-plane conductivity by means of direct current (DC) and alternating current (AC) electrical transport properties.

2. MATERIALS AND METHODS

2.1. Preparation of PEDOT:PSS-MWCNT Nanocomposites. A poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) 1.3% w/w water solution was purchased from Sigma-Aldrich and multiwalled carbon nanotubes (MWCNTs) were purchased from Cheap Tubes (length: 10–30 μm and outer diameter: <8 nm). The corresponding amounts of MWCNTs (0, 0.1, 1, and 10%) were added into the PEDOT:PSS 1.3% w/w water solution and kept stirred. Then, the mixed suspension was exposed to ultrasonic treatment working with 30 W for 30 min. The resulting solution was spin-coated onto an ITO/glass substrate at 1000 rpm for 30 s and 2000 rpm for another 30 s. In this work, the studied MWCNT's fractions were 0, 0.1, 1, and 10%, named as PP-X with $X = 0, 0.1, 1$, and 10%, respectively.

2.2. Characterization. X-ray reflectometry (XRR) and grazing incidence small-angle X-ray scattering (GI-SAXS) were performed using Rigaku Ultima IV diffractometer with Cu $K\alpha$ radiation working in parallel beam configuration. XRR patterns were used to estimate the critical angles, and GI-SAXS out-of-plane patterns were collected in the $q_z = 0.01$ – $0.1 \text{ \AA}^{-1}$ range at a fixed incident angle of 0.2° with respect to the critical angle. Optical transmittance measurements were performed using a Thorlabs CCS200 wide-range spectrometer (200–1000 nm). In-plane and out-of-plane confocal Raman spectroscopy and atomic force microscopy (AFM) in the AC mode were performed using WITec alpha300-RA equipment. Raman spectra for all samples were collected using an excitation laser wavelength of 532 nm and the laser power was adjusted at $\sim 5 \text{ mW}$ to avoid PEDOT:PSS decomposition. In-plane confocal Raman images were obtained for a $20 \times 20 \mu\text{m}^2$ total area utilizing a grid of 75×75 points. Out-of-plane confocal Raman microscopy images were performed for a $5 \times 5 \mu\text{m}^2$ total area. Out-of-plane DC conductivity versus temperature measurements were obtained with a Keithley 2400 sourcemeter using a two-probe configuration and a Janis CCS-150 cryogenic system in the temperature range 250–296 K. AC impedance spectroscopy analysis was performed using a Gamry Reference 3000 impedance analyzer at $T = 296 \text{ K}$. The applied AC voltage amplitude was 10 mV in the 0.1 Hz to 1 MHz frequency regime with applied $V_{\text{DC}} = 0$ –2 V DC voltages.

3. RESULTS AND DISCUSSION

3.1. X-ray Reflectometry. X-ray reflectometry (XRR) curves for PP-X with $X = 0, 0.1, 1$, and 10% are shown in Figure 1a. XRR data were fitted using a simple model based in a PEDOT:PSS-MWCNTs layer followed by an ITO layer, both on top of a glass substrate, as implemented in GlobalFit software.²⁶ The XRR data fittings showed a similar behavior for all MWCNT loadings denoted by a drastic lowering of the reflected intensity in relation to the presence of two layers: one ascribed to a lower-density PEDOT:PSS-MWCNT and the other to a higher-density ITO layer. The most relevant parameters of XRR data fittings are shown in Table 1. In all cases, the ITO layer showed no drastic variations from $\rho \sim 5 \text{ g cm}^{-3}$ densities, $R \sim 4$ – 6 nm root mean square (rms) roughness, and $d \sim 120$ – 140 nm thickness. On the contrary, the PEDOT:PSS-MWCNTs layer showed no deviations from $\rho \sim 1.2$ – 1.8 g cm^{-3} densities, $R \sim 2.7$ – 2.9 nm rms roughness,

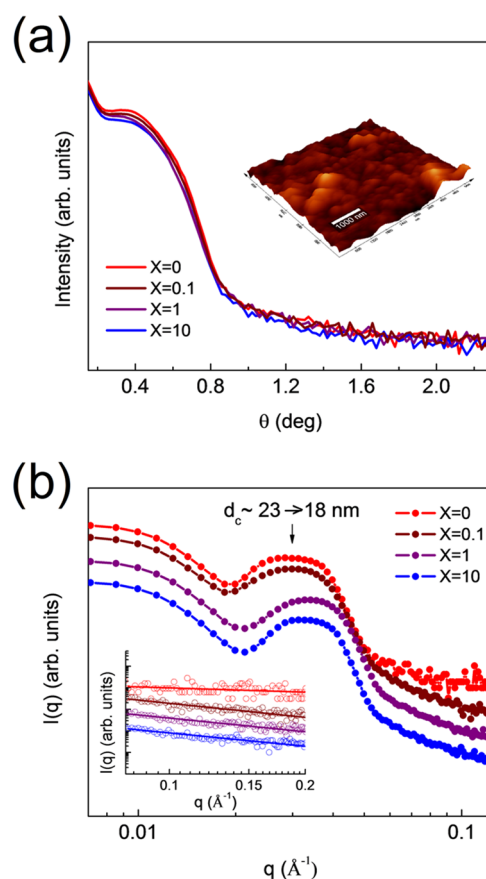


Figure 1. (a) X-ray reflectometry (XRR) and (b) grazing incidence small-angle X-ray scattering (GI-SAXS) for PP-X with $X = 0, 0.1, 1$, and 10%. Inset in (a) shows atomic force microscopy (AFM) topography for PP-10% as an example and inset in (b) shows the high- q region and power law fittings.

and $d \sim 180$ – 200 nm thickness. However, it is important to remark that a $d \sim 200 \text{ nm}$ thickness is near the resolution limit ($d \sim 1/\Delta\theta$) of our XRR data, suggesting that these values could be underestimated. On the contrary, there is a slight but clear trend from $\rho \sim 1.8$ to 1.2 g cm^{-3} , with increasing amounts of MWCNT loadings. This is suggesting that the lower density of the resulting PEDOT:PSS-MWCNT films could be possibly due to the increasing concentration of “empty spaces” associated with the addition of MWCNTs. To have a local approach to the polymeric film surface, an atomic force microscopy (AFM) topography image is also displayed for PP-X with $X = 10\%$ as an example in Figure 1a, inset.

3.2. Grazing Incidence Small-Angle X-ray Scattering. Grazing incidence small-angle X-ray scattering (GI-SAXS) curves for PP-X with $X = 0, 0.1, 1$, and 10% are shown in Figure 1b. In all cases, the GI-SAXS curves showed a well-distinguished relative maximum at the mid- q region, which could be roughly related with mean correlation distances (d_c) using the equation $d_c \sim 2\pi/q_{\text{max}}$. A slight increase in the position of the maximum was observed from $q_{\text{max}} \sim 0.028$ to $0.036 \text{ \AA}^{-1}$, in relation to a decrease from $d_c \sim 23 \pm 3$ to $18 \pm 3 \text{ nm}$ with increasing MWCNT loadings. These mean correlation distances could be attributed to a certain degree of self-organization among the chain fibers, leading to the formation of “empty spaces” between polymer fibers, as already observed.^{27–29} The slight decrease in d_c could be related to the approximation of the polymer fibers promoted by the

Table 1. X-ray Reflectometry (XRR) and Grazing Incidence Small-Angle X-ray Scattering (GI-SAXS) Analysis for PP-X Films with $X = 0, 0.1, 1$, and $10\%^a$

		ρ (g cm $^{-3}$)	R (nm)	d (nm)	d_c (nm)	P
$X = 0$	PP-X	1.82 (4)	2.74 (10)	187.4 (8)	23 (3)	1.2 (2)
	ITO	5.58 (10)	5.0 (2)	138.6 (11)		
$X = 0.1$	PP-X	1.42 (6)	2.80 (15)	193.9 (9)	22 (3)	2.5 (1)
	ITO	5.05 (8)	4.40 (17)	135.6 (10)		
$X = 1$	PP-X	1.58 (7)	2.84 (17)	196.6 (12)	18 (3)	2.7 (1)
	ITO	5.05 (9)	4.54 (19)	120.9 (11)		
$X = 10$	PP-X	1.20 (3)	2.8 (2)	196.1 (5)	18 (3)	2.6 (1)
	ITO	4.89 (8)	4.23 (14)	124.5 (8)		

^aDensity (ρ), roughness (R), and thickness (d) fitted parameters were obtained from XRR data using GlobalFit software from Rigaku.²⁴ The correlation distances (d_c) were estimated using $d_c \sim 2\pi/q_{\max}$ and the Porod exponents (P) were obtained from the power law fitting at the high- q region.

increasing interactions with the addition of MWCNTs. The high- q region of GI-SAXS data showed good fitting with a typical $\sim q^{-P}$ power law, as shown in Figure 1b, inset. The power exponent (P) values at the high- q region ($0.07 < q < 0.2 \text{ \AA}^{-1}$) were $\sim 1.2, 2.5, 2.7$, and 2.6 for $X = 0, 0.1, 1$, and 10% , respectively, as already observed for PEDOT:PSS samples.^{27,28,30} The increase in the power exponent (P) with MWCNT addition could be attributed to the formation of more tightly compact structures, in analogy to those formed for PEDOT:PSS in water solution.^{27,30} The increasing MWCNT loadings could be promoting the interaction with PEDOT:PSS fibers, probably via π - π interactions, thus leading to more compact structures, also in agreement with the decrease of the mean correlation length from 23 ± 3 to 18 ± 3 nm, as discussed above.

3.3. Optical Transmittance Spectroscopy. Optical transmittance spectra for PP-X films with $X = 0, 0.1, 1$, and 10% are shown in Figure 2. The transmittance measurements

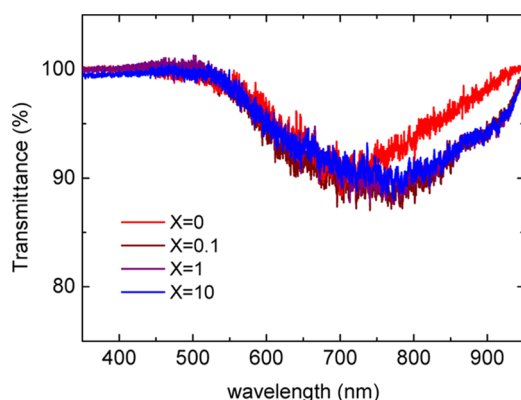


Figure 2. Optical transmittance spectra for PP-X films with $X = 0, 0.1, 1$, and 10% . The transmittance measurements were obtained by subtracting the ITO/glass substrate references to evaluate only the transmittance of PP-X films.

were obtained by subtracting the ITO/glass substrate references to evaluate only the transmittance of PP-X films. The optical transmittance of $X = 0\%$ is the highest; however, the transmittance of MWCNT loaded films ($X = 0.1, 1$, and 10%) showed only a slight decrease in the overall transmittance. The major absorption of the PEDOT:PSS layers is in the $\lambda = 550$ – 900 nm range, as already observed in previous reports.^{10,31} The slight decrease in the transmittance due to

MWCNT additions is of great relevance for the potential application as electrode in solar cells.

3.4. In-Plane and Out-of-Plane Confocal Raman Microscopies. In-plane confocal Raman spectra at selected PEDOT:PSS-rich and MWCNTs-rich zones for PP-X with $X = 0, 0.1, 1$, and 10% are shown in Figure 3. The Raman spectra

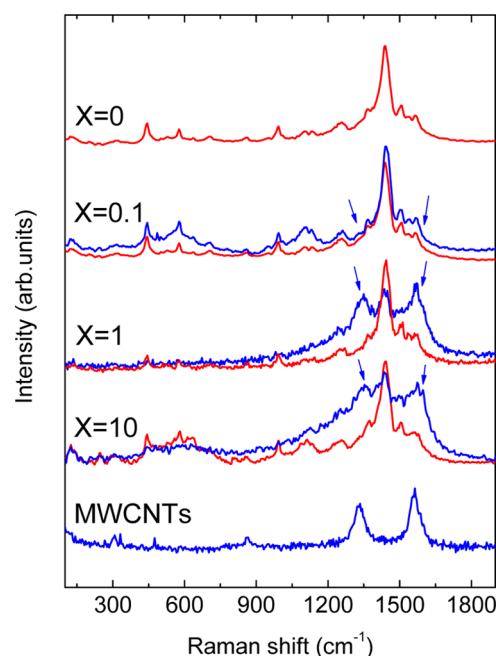


Figure 3. Raman spectra at selected areas of PEDOT:PSS-rich (red lines) and MWCNT-rich (blue lines) zones for PP-X with $X = 0, 0.1, 1$, and 10% and MWCNT reference.

for the PEDOT:PSS-rich (red) and MWCNTs-rich (blue) zones were defined by filtering the peak at $\sim 1436 \text{ cm}^{-1}$ corresponding to C=C stretching mode of PEDOT:PSS and the peak at $\sim 1580 \text{ cm}^{-1}$ corresponding to the G band of MWCNTs, respectively. The Raman spectra shown in Figure 3 correspond to the in-plane confocal Raman images (Figure 4) for PEDOT:PSS-rich (red) and MWCNTs-rich (blue) zones for PP-X with $X = 0, 0.1, 1$, and 10% . An additional Raman spectrum of the MWCNT reference is also shown in Figure 3. PEDOT:PSS typical modes are situated at $\sim 700, 990, 1100$ – $1135, 1258, 1366$, and 1434 – 1444 cm^{-1} , ascribed to C–S–C bending, C–C antisymmetrical stretching, C–O–C stretching, C–C stretching, C–C inter-ring stretching, and C=C

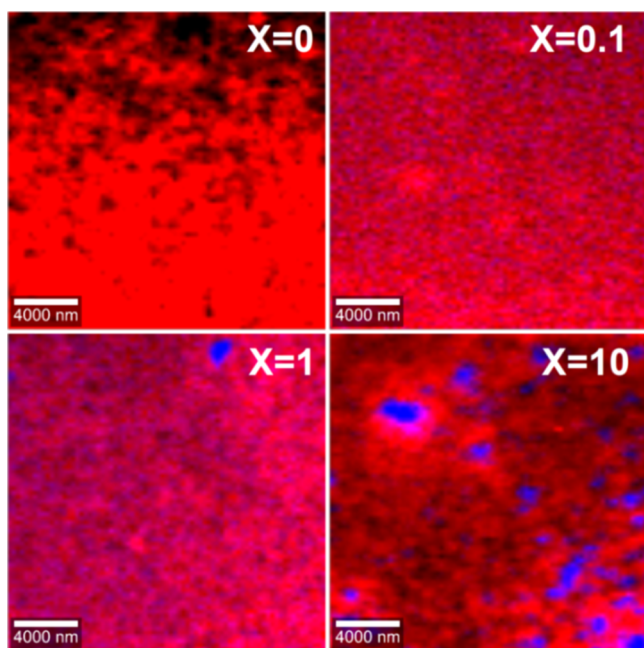


Figure 4. In-plane profile confocal Raman microscopy scan for PP-*X* with *X* = 0, 0.1, 1, and 10%. The PEDOT:PSS-rich (red) and MWCNT-rich (blue) zones correspond to the maximization of the relative intensity of the 1436 cm^{-1} peak and G-band vibrational modes, respectively.

symmetric stretching of the aromatic modes, respectively. Two additional peaks at 1509 and 1567 cm^{-1} are attributed to C=C asymmetrical stretching modes.^{32,33} On the contrary, MWCNTs typical peaks at 1350 and 1580 cm^{-1} are ascribed to D and G bands, respectively.³⁴ Raman spectra for *X* = 0.1% showed similarities between PEDOT:PSS-rich and MWCNTs-rich zones but for a low intensity shoulder at 1350 cm^{-1} ascribed to the D mode of MWCNTs, in agreement with a highly diluted system. However, the occurrence of both D and G bands of MWCNTs was more evident for *X* > 0.1% due to the higher concentration. It is important to remark that there is a clear contribution of both phases on each PEDOT:PSS or MWCNT-rich zones, especially for *X* = 0.1 and 1%, suggesting good homogeneity and high degree of mixing, even at the sub-micrometer scale. In the case of *X* = 10%, the larger concentration of MWCNTs leads to the appearance of blue well-defined zones in Figure 4, in relation to the agglomeration of MWCNTs, evidencing a declining in the homogeneity of PP-*X* nanocomposites. At first sight, there are no drastic modifications on the position of PEDOT:PSS vibrational modes for none of the zones. However, an approach to the Raman spectra for both PEDOT:PSS and MWCNT-rich zones in the 1200–1600 cm^{-1} region is shown in Figure 5a to have a better insight. The peak ascribed to the C=C stretching mode of PEDOT:PSS showed different locations: at 1434 and 1444 cm^{-1} , for the MWCNT-rich and the PEDOT:PSS-rich zones, respectively, as shown in Figure 5a. The shift from ~1444 to 1434 cm^{-1} could be in agreement with the transformation of PEDOT from a benzoid to a quinoid structure,^{35,16} whose structural models are shown in Figure 5c. Our results indicate that there is an increase in the population of quinoid conformation in the vicinities of MWCNTs, which could be related to an enhancement in the conductivity.³⁵ The same trend was observed for *X* = 1% and could also be extrapolated

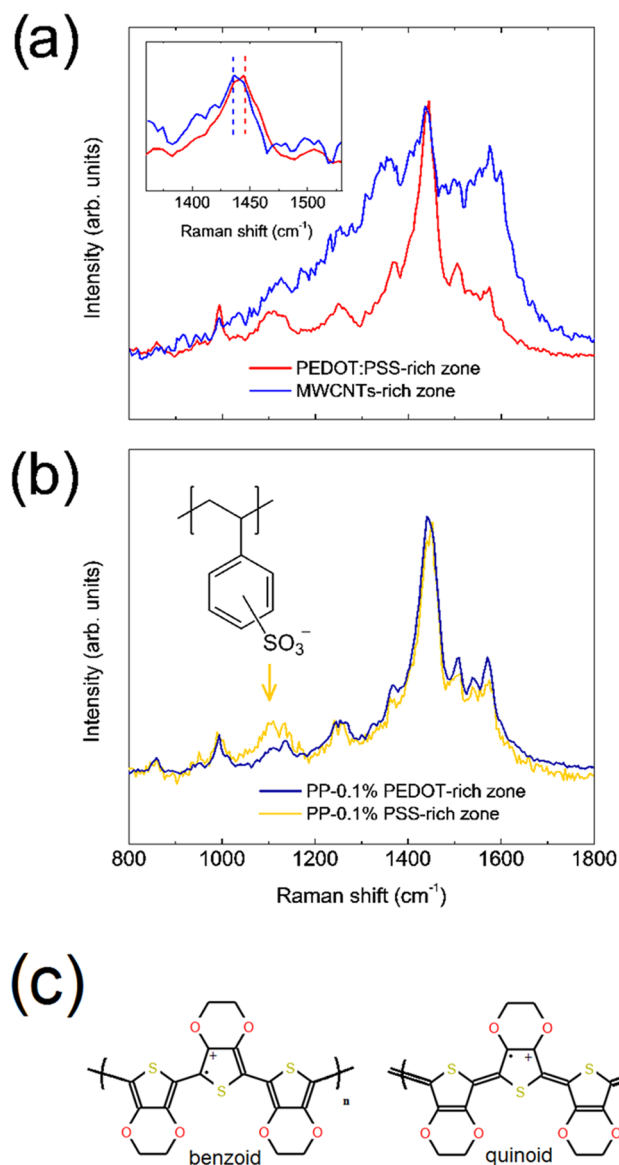


Figure 5. (a) In-plane confocal Raman microscopy spectra at selected PEDOT:PSS-rich and MWCNTs-rich zones for PP-*X* with *X* = 10%. The inset shows a zoom of the peak shift ascribed to benzoid-to-quinoid transition. (b) Out-of-plane confocal Raman microscopy spectra for PEDOT-rich (blue) and PSS-rich (yellow) zones for PP-*X*, with *X* = 0.1%. The inset shows the structure of the PSS monomer. (c) PEDOT benzoid and quinoid structural conformations.

to *X* = 0.1%, but in the latter, the low amounts of MWCNTs hamper the observation of this Raman shift with clarity. It is important to remark that *X* = 0% showed the position of the C=C vibrational mode at ~1442 cm^{-1} , suggesting that the presence of MWCNTs clearly leads to the increment of the PEDOT quinoid conformation at expenses of the benzoid configuration.

Out-of-plane profile confocal Raman microscopy images for PP-*X* with *X* = 0, 0.1, 1, and 10% are shown in Figure 6. The confocal Raman microscopy images are limited, in an ideal case, to ~300 nm optical resolution, leading to an overestimation of those dimensions below that dimension. In all cases, the thickness estimation using XRR analysis showed a PP-*X* thickness of about 190 nm, but, as stated above, the films thickness will be detected above 300 nm in our confocal Raman

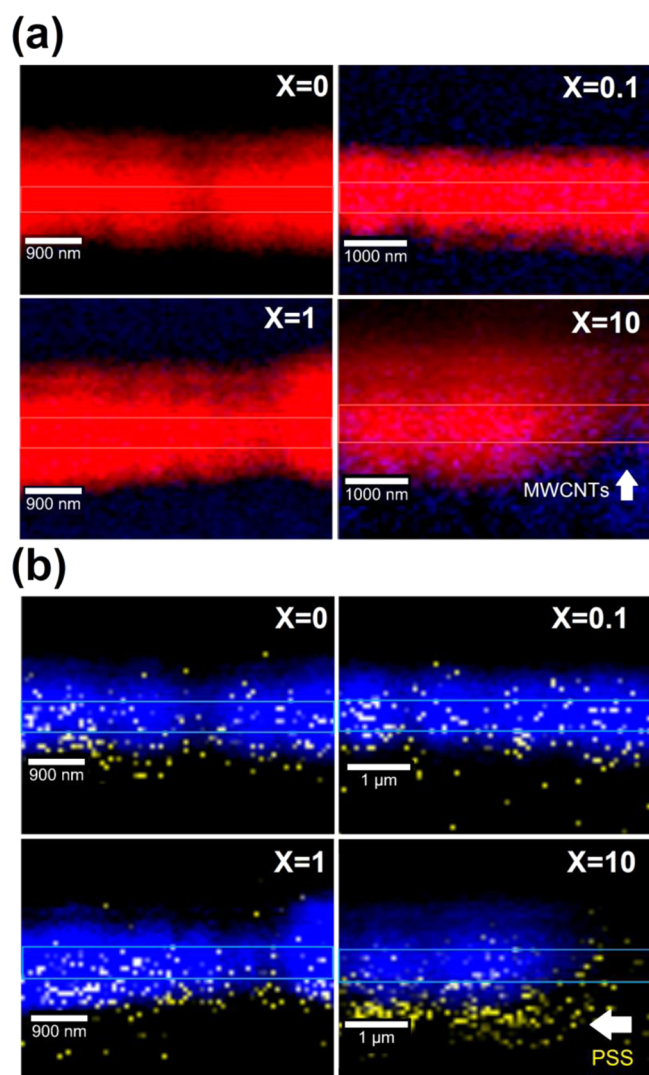


Figure 6. Out-of-plane confocal Raman microscopy scan for PP-X with $X = 0, 0.1, 1$, and 10% . (a) PEDOT:PSS-rich (red) and MWCNT-rich (blue) zones correspond to the maximization of the relative intensity of the peaks at 1436 cm^{-1} ($\text{C}=\text{C}$, PEDOT) and 1350 cm^{-1} (D band, MWCNTs), respectively. (b) PEDOT-rich (blue) and PSS-rich (yellow) zones correspond to the maximization of the relative intensity of the peaks at 1436 cm^{-1} ($\text{C}=\text{C}$, PEDOT) and 1090 cm^{-1} ($\text{S}=\text{O}$, sulfonate group of PSS), respectively.

microscopy images. As a guide to the eye, we framed the PP-X film zone by using two straight lines at the optical limit resolution, that is, $\sim 300\text{ nm}$, as shown in Figure 6. We can also distinguish two other zones associated with the interface with air at the top and the interface with ITO at the bottom of the marked frame. The out-of-plane confocal Raman microscopy images displayed in Figure 6a were filtered to obtain PEDOT:PSS-rich and MWCNTs-rich zones. The PEDOT:PSS-rich (red) and MWCNT-rich (blue) zones were also obtained by filtering the $\text{C}=\text{C}$ stretching mode of PEDOT and the G band of MWCNTs, respectively, as discussed above. The low concentration of MWCNTs ($X < 10\%$) showed mostly PEDOT:PSS-rich zones, but the appearance of blue spots in random locations suggests that the MWCNTs are more or less homogeneously distributed for PP-X films with $X < 10\%$. For the $X = 10\%$ composition, a segregated blue zone is observed, probably due to the presence of agglomerated

MWCNTs, as also evidenced by the in-plane confocal Raman microscopy images. Out-of-plane confocal Raman microscopy spectra for the selected PEDOT:PSS-rich zone at the PP-X film zone and at the ITO interface for a selected composition ($X = 0.1\%$) are shown in Figure 5b. We observe a splitting of the $\text{C}=\text{C}$ stretching mode ascribed to PEDOT originally at $\sim 1440\text{ cm}^{-1}$ toward 1440 and 1454 cm^{-1} for the PP-X films at the ITO interface zone. However, this Raman splitting is not precisely in agreement with a benzoid-to-quinoid conformation transition. Interestingly, we also observe at the ITO interface, an increase in the relative intensity of the Raman peak at $\sim 1090\text{ cm}^{-1}$, which is usually attributed to vibrational modes of PSS sulfonate groups.³⁶ This suggests that the PSS concentration is relatively high at the ITO interface, probably due to its charged nature, thus enhancing the interaction with the ITO interface. The out-of-plane confocal Raman microscopy images displayed in Figure 6b were filtered to obtain PEDOT-rich and PSS-rich zones for our film specimens. The PEDOT-rich (blue) and PSS-rich (yellow) zones were also obtained by filtering the $\text{C}=\text{C}$ stretching mode of PEDOT and the sulfonate stretching mode of PSS, respectively. There is clear evidence that the increasing amounts of MWCNTs, especially for 10% loadings, lead to an enrichment of PSS at the ITO interface. The formation of PSS-rich zones close to the ITO interface could be a strong influence to the decline of the charge carrier injection from carbon nanotube-doped PEDOT:PSS into the ITO layer.

3.5. DC Electrical Transport. DC out-of-plane resistance and the corresponding conductivities versus temperature for PP-X, with $X = 0, 0.1, 1$, and 10% in the temperature range of $250\text{--}296\text{ K}$, are shown in Figure 7. A quasi-temperature-independent behavior for out-of-plane conductivity was observed for all PP-X samples in the temperature regime analyzed. Only a slight decrease in conductivity was observed for $X = 10\%$, in agreement with a small semiconducting behavior. In all cases, a linear behavior was observed in the $I\text{--}V$ curves obtained at room temperature in Figure 7a, inset, suggesting no drastic deviations from an ohmic behavior. The highest out-of-plane conductivities were observed for lower amounts of MWCNT loadings, exhibiting the maximum conductivity for the $X = 0.1\%$ composition. Our out-of-plane conductivity values ($\sim 10^{-6}\text{ S cm}^{-1}$) are in the order of those reported in bibliography.⁷ Meanwhile, the $X = 10\%$ composition showed a drastic decrease in the out-of-plane conductivity, even below the conductivity observed for unloaded ($X = 0\%$) polymer films. The improvement of the out-of-plane conductivity for the films with lower MWCNT concentration could be in agreement with the optimization of the interaction between PEDOT:PSS with MWCNTs. Our confocal Raman microscopy analysis showed an increment in the population of the PEDOT quinoid structure in the vicinities of MWCNTs, suggesting that the enhancement on this interaction could lead to an increase in the electrical conductivity. The good dispersion of MWCNTs in the polymeric matrix for $X = 0.1$ and 1% is probably responsible for the improvement in the out-of-plane conductivity. The drastic decrease in the conductivity for $X = 10\%$ could be due to the MWCNT aggregation, which is in accordance with the confocal Raman image in Figure 4. Nevertheless, our out-of-plane confocal Raman microscopy analysis also showed the presence of poor-conducting PSS at the ITO interface. This could explain the high anisotropy observed for the out-of-plane conductivities, with respect to the in-plane configuration.

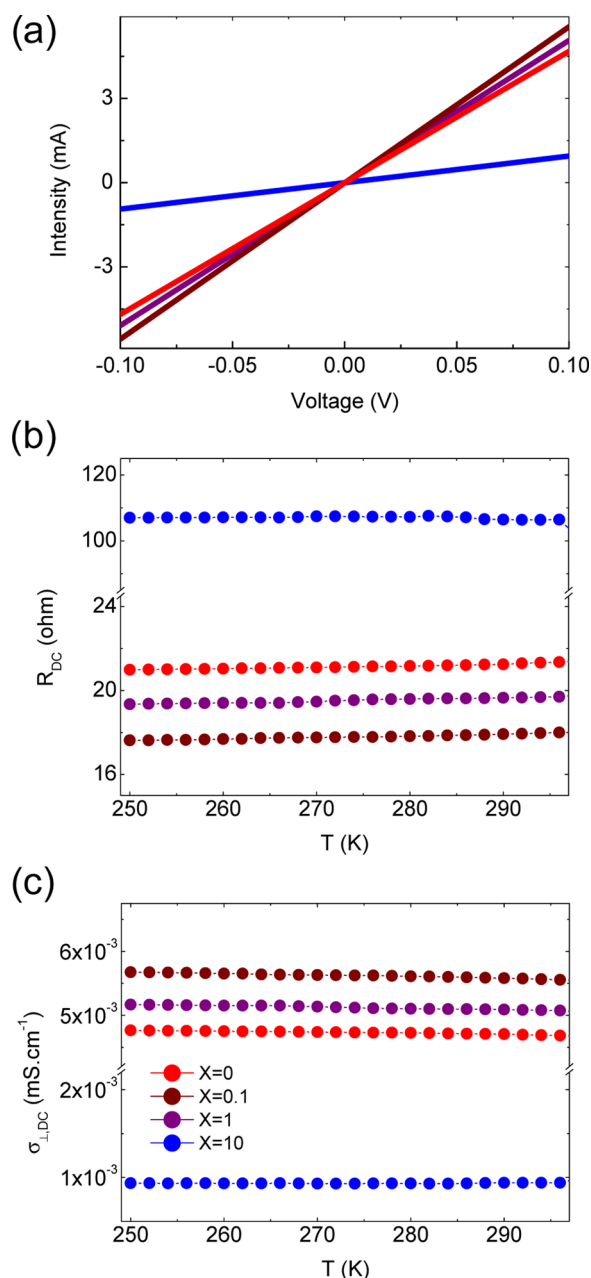


Figure 7. (a) I – V curves obtained at room temperature, (b) DC resistance (R_{DC}), and (c) DC out-of-plane conductivity ($\sigma_{\perp,DC}$) vs temperature for PP- X with $X = 0, 0.1, 1$, and 10%.

3.6. AC Electrical Transport. Impedance modulus dependences with frequency plots at different applied DC voltages for PP- X with $X = 0, 0.1, 1$, and 10% are shown in Figure 8. A frequency-independent impedance behavior for PEDOT:PSS-MWCNT films was observed for lower MWCNT loadings ($X = 0$ –1%) in a wide frequency range from 10^5 to 10^{-1} Hz. In the case $X = 10\%$, a small capacitive behavior was observed, which is evidenced by an increase in the impedance modulus at high frequencies. A progressive decrease in the impedance modulus was observed with increase in applied DC voltage for all compositions. To obtain a more quantitative insight on the AC electrical transport, impedance data was fitted using a circuit model composed of the parallel combination of a resistor (R) and a nonideal capacitor called constant phase element (CPE), where impedance can be defined as

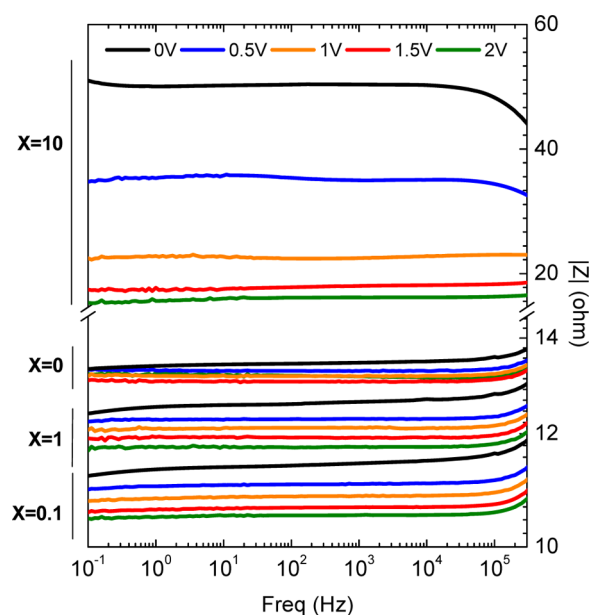


Figure 8. Impedance modulus vs frequency at different applied DC voltages ($V_{DC} = 0$ –2 V) for PP- X , with $X = 0, 0.1, 1$, and 10%.

$$Z_{CPE} = \frac{1}{Q_0 \omega^n} e^{-j(\pi/2)n}$$

The nonideal capacitive contribution to the electrical transport was observed clearly only for $X = 10\%$, being negligible for $X = 0, 0.1$, and 1%, in accordance with a near-ohmic behavior. The frequency-independent impedance behavior could be a result of the formation of a compact PEDOT:PSS-MWCNT layer on top of the ITO electrode. This near-ohmic behavior is in agreement with the DC analysis discussed in the previous section, as also previously observed for other PEDOT:PSS layers deposited on metal substrates.^{37,38} The fitted resistance values and the corresponding AC out-of-plane conductivities versus the applied DC voltage are shown in Figure 9a,b, respectively. At zero bias, the AC out-of-plane conductivities showed very similar results to those obtained using DC out-of-plane conductivities. A linear increase in conductivity was observed with increasing DC bias for $X < 10\%$, showing a small but positive slope. This is in agreement with a near-ohmic behavior, as already discussed above. However, a nonlinear increase in conductivity was observed with increasing DC bias for $X = 10\%$ showing a threshold DC voltage at about $V \sim 1$ –2 V, upon which an increase in conductivity was observed. The high amounts of MWCNT loadings probably lead to a deviation of an ohmic behavior, in agreement with the increase in the capacitive behavior. The MWCNT aggregation and the enrichment of poor-conducting PSS at the ITO interface, especially observed for higher loadings ($X = 10\%$), could be responsible for both the decrease in the electrical out-of-plane conductivity and the capacitive behavior.

4. CONCLUSIONS

In this report, we show the effect of MWCNT doping on the structure and out-of-plane conductivity of PEDOT:PSS/ITO electrodes for solar cell applications. For the first time, we showed in-plane and out-of-plane profile confocal Raman microscopy characterizations of these electrode materials. We found interesting structural conformation modifications of PEDOT at both the MWCNTs and the ITO interface, in

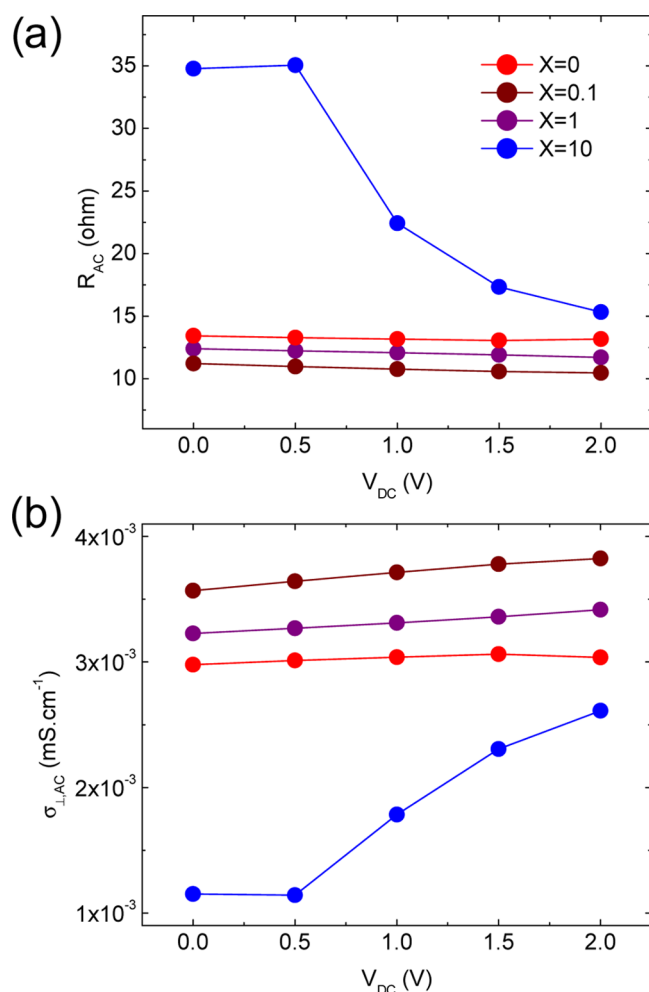


Figure 9. (a) Fitted AC resistance (R_{AC}) and (b) AC out-of-plane conductivity ($\sigma_{\perp,AC}$) vs applied DC voltage for PP-X with $X = 0, 0.1, 1$, and 10%.

correlation with the electrical transport properties. Modifications in the PEDOT benzenoid and quinoid conformations were observed in the vicinities of the MWCNT interface and enrichment of PSS concentration at the indium tin oxide (ITO) electrode interface. A near-ohmic behavior was observed in all cases, and an increase in the out-of-plane conductivity was observed for low amounts (0.1%) of MWCNT doping, as usually observed for the in-plane conductivity. However, for higher amounts (10%) of MWCNT loadings, the enrichment of the poor-conducting PSS at the interface with the ITO layer could be responsible for the decrease in electrical transport.

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Notes

The authors declare no competing financial interest.

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