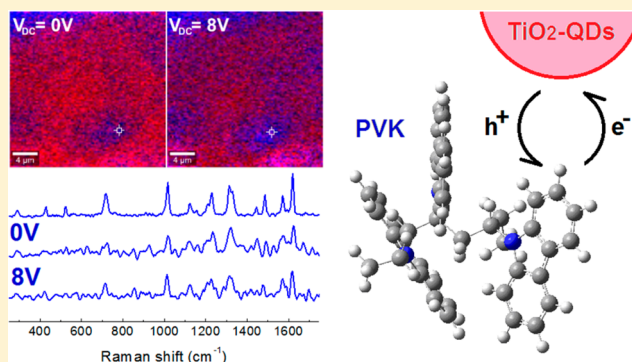


Raman and Impedance Spectroscopy under Applied Dc Bias Insights on the Electrical Transport for Donor:Acceptor Nanocomposites Based on Poly(vinyl carbazole) and TiO₂ Quantum Dots

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ABSTRACT: In this report, we studied Raman and impedance spectroscopy under applied dc bias for poly(vinyl carbazole)-titania quantum dots (PVK:TiO₂-QDs) nanocomposites to understand the electrical transport in this donor:acceptor system as promising active layer materials for polymeric solar cells. The nanocomposites were synthesized using a novel strategy involving the sol–gel method via *in situ* water vapor flow diffusion in the polymer host leading to ~3–8 nm TiO₂ quantum dots embedded in PVK with excellent homogeneity. Raman spectroscopy was used to monitor the presence of charge carriers in the organic semiconductor for PVK:TiO₂-QDs with different TiO₂ quantum dots compositions with and without applied dc voltage. The joint study of confocal Raman spectroscopy supported by theoretical simulations together with impedance spectroscopy under applied dc voltage could give us a major approach to understand the electrical transport mechanism of these hybrid donor:acceptor nanocomposites.



1. INTRODUCTION

In the recent years, there has been a growing interest in the preparation of organic donor–acceptor polymer composites due to their use in active layers materials for polymer solar cells.^{1–3} One of the most popular donor:acceptor polymer composites used for this purpose is poly(vinyl carbazole) (PVK) polymer as donor and [6,6]-phenyl-(C71 or C61)-butyric acid methyl ester (PC61BM or PC71BM) fullerene as acceptors.^{4,5} These fullerene-derived acceptor materials are one of the most popular acceptor materials due to their high electron affinity and mobility. However, these acceptor materials have also shown disadvantages regarding the low absorption in the visible spectra and high cost of fabrication, making them nonideal candidates for technological applications. For this reason, in the past few years, nonfullerene acceptors have been studied in order to obtain higher light absorption and lower costs of fabrication.^{6–10} The preparation of conjugated polymers composites using inorganic nanoparticles fillers such as the low cost and nontoxic titanium oxide (TiO₂) nanoparticles as acceptors has also been already reported.^{11–14} Recently, the preparation of PVK:TiO₂ nanocomposites were prepared by *in situ* polymerization in the presence of TiO₂ nanotubes for solar cell applications.¹⁵ However, the preparation of these polymer nanocomposites via *in situ* growth of oxide quantum dots has not been reported yet and could be of great interest for the improvement of the electrical properties. Besides this, we have also chosen this particular system to study the presence of PVK charge carriers by means of Raman spectroscopy under applied dc voltage. For

instance, the presence of Raman TiO₂ quantum dots acceptors with almost no Raman peaks above 750 cm^{−1} could facilitate the interpretation of Raman spectra modifications of PVK donor under the presence of an applied dc voltage. To the best of our knowledge, there are few reports regarding PVK-based composites structural modifications under applied bias to understand the electrical transport mechanism of the electron–hole recombination processes.^{13,16–18} In this report, we show for the first time, experimental and theoretical evidence of PVK structural modifications due to charge carrier formation in PVK:TiO₂-QDs nanocomposites under the presence of applied dc bias by means of confocal Raman microscopy in strong correlation with impedance spectroscopy analyses. Thus, we are showing experimental evidence supported by first-principles calculations, that Raman spectroscopy can be a powerful tool to understand PVK electrical transport mechanism under applied dc bias.

2. MATERIALS AND METHODS

2.1. Synthesis of PVK–TiO₂ Nanocomposites. The synthesis of PVK–TiO₂ nanocomposites was based on previously reported sol–gel synthesis via water vapor flow diffusion, as recently reported.¹⁹ Poly(9-vinyl carbazole) (PVK) (0.3 g) purchased from Sigma-Aldrich with average *M_w* ~ 1 100 000, were suspended in 50 mL of tetrahydrofuran (THF)

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and kept stirred at $T = 70\text{ }^{\circ}\text{C}$. When the suspension kept homogeneously colorless, 1 mL of deionized water was added slowly dropwise under stirring at 500 rpm for 30 min. The corresponding amount of titanium tetrapropoxide (TTP), 98% purchased from Sigma-Aldrich, was added to the PVK suspension and kept stirred at $T = 70\text{ }^{\circ}\text{C}$ until dryness. The resulting yellow powder was grinded and exposed to deionized water vapor at $T = 80\text{ }^{\circ}\text{C}$ with a vapor flow of $\sim 1\text{ mL/min}$ during 16 h. All compositions were finally dried at $T = 80\text{ }^{\circ}\text{C}$ under vacuum for 7 h to eliminate residual water and propanol generated from the hydrolysis process. The dried powders were finally pressed at 50 kN/cm^2 to form pellets. The samples that corresponded to 10%, 30%, 50% and 70% of the weight fraction of TiO_2 quantum dots were named as x10, x30, x50 and x70, respectively.

2.2. Characterization and Computational Methods.

High-resolution transmission electron microscopy (HR-TEM) was performed in order to study the size and morphology of PVK: TiO_2 -QDs nanocomposites using a JEOL 2100 instrument working under a 200 kV voltage. Selected area electron diffraction (SAED) and energy dispersive spectroscopy (EDS) analyses were performed to study the local structure and chemical composition, respectively. UV-vis measurements were obtained with Ultrospec 3100 Pro spectrophotometer working in the wavelength range of 350–650 nm using chloroform as solvent. In order to obtain Raman spectra simulation, we performed density functional calculations (DFT)^{20,21} with the hybrid exchange correlation potential B3LYP^{22–25} for a 6-31++ G(d,p) basis set, utilizing Gaussian 09.²⁶ We also performed confocal Raman microscopy obtained using WITec Alpha 300-RA equipment. Raman spectra for all samples were collected using an excitation laser wavelength of 532 nm. For each case, a set of 20 spectra with 0.2 s integration time were averaged. Confocal Raman images were obtained for a $(25 \times 25)\text{ }\mu\text{m}^2$ total area utilizing a grid of (90×90) points. Raman spectra were additionally collected with and without applied voltage (8 V) for x10, x30, and x50. Ac impedance spectroscopy analysis was performed for the PVK- TiO_2 pellets using stainless steel electrodes with a Gamry Reference 3000 impedance analyzer at $T = 300\text{ K}$. The applied ac voltage amplitude was 10 mV in the 1 Hz–1 MHz frequency regime with applied dc voltages ranged between $V_{\text{dc}} = 0$ and 8 V.

3. RESULTS AND DISCUSSION

3.1. Transmission Electron Microscopy. Transmission electron microscopy (TEM) images for x50 nanocomposite at different magnifications are shown in Figure 1a,b. The excellent homogeneity of our nanocomposites is evident, as can be observed in Figure 1a. The presence of nanocrystalline TiO_2 quantum dots with $\sim 3\text{--}8\text{ nm}$ size can be evidenced in the higher magnification TEM image shown in Figure 1b. The *in situ* growth of TiO_2 quantum dots into the PVK host revealed the formation of polyhedral shaped nanocrystals with moderate degree of coalescence. These TiO_2 quantum dots exhibited sharp edges and well-defined grain boundaries, as shown in Figure 1b. High resolution TEM image for x50 nanocomposite is shown in Figure 1c, for which a nondefect nanocrystalline array is observed. Electron dispersive spectroscopy (EDS) analysis for x50, showed in Figure 1d, indicates that the composition of our nanocomposites consists in carbon and nitrogen ascribed to the presence of PVK and oxygen and titanium ascribed to the presence of TiO_2 -QDs, respectively. In addition, the inset of Figure 1d, selected area electron

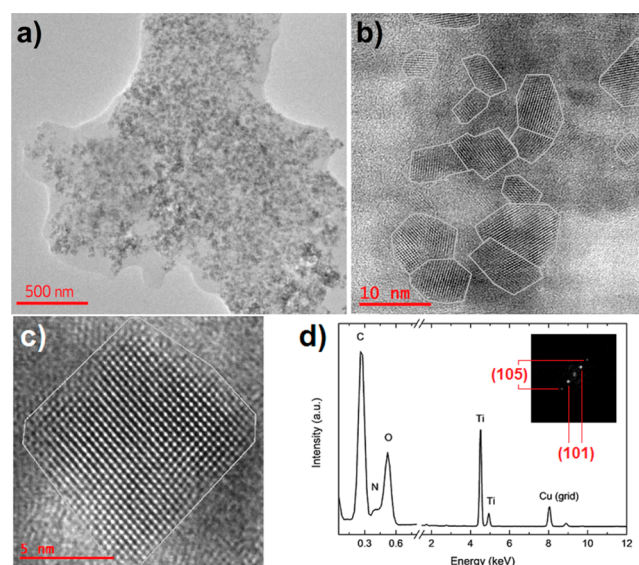


Figure 1. (a, b) Transmission electron microscopy (TEM) images at different magnifications, (c) high resolution TEM images, and (d) electron dispersive spectroscopy (EDS) for x50 nanocomposites. Selected area electron diffraction (SAED) analysis for x50 nanocomposites is shown in the inset to part d.

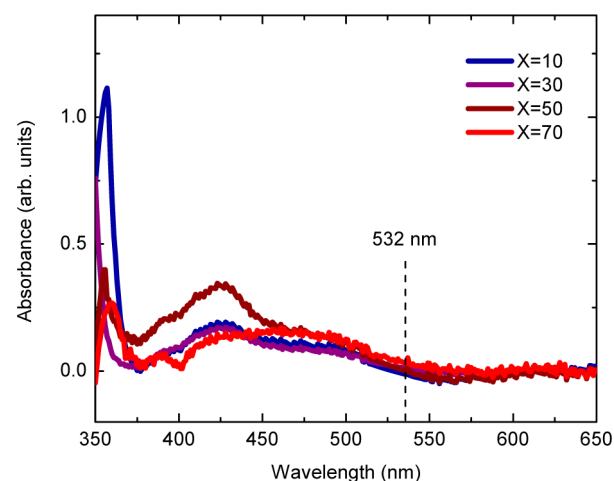


Figure 2. UV/vis absorbance spectra for x10, x30, x50, and x70 nanocomposites in chloroform. The dashed line indicates the 532 nm wavelength used for off-resonance Raman experiment.

diffraction (SAED) analysis revealed the presence of two of the more intense reflections spots (101) and (105) corresponding to TiO_2 anatase polymorph, as also observed for other TiO_2 quantum dots nanocomposites.²⁷

3.2. UV/Vis Spectroscopy. UV/vis absorbance plots for PVK: TiO_2 -QDs nanocomposites dispersed in chloroform are shown in Figure 2. It is well-known that the absorption spectra for pure PVK polymer showed a peak at $\lambda \sim 350\text{--}360\text{ nm}$ ascribed to $\pi\text{--}\pi^*$ optical transitions in pendant carbazole moieties of PVK.¹⁵ In our case, these peaks decrease its absorption relative intensity, as expected with decreasing PVK concentration. However, x10, x30, and x50 showed additional broad peaks located at $\lambda \sim 390$ and 430 nm , that could be possibly attributed to charge-transfer transitions, as already observed in iodine-doped carbazole samples.²⁸ It is also important to note that these peaks are in the same wavelength with those ascribed to PVK excimers emission.^{29–32} Moreover,

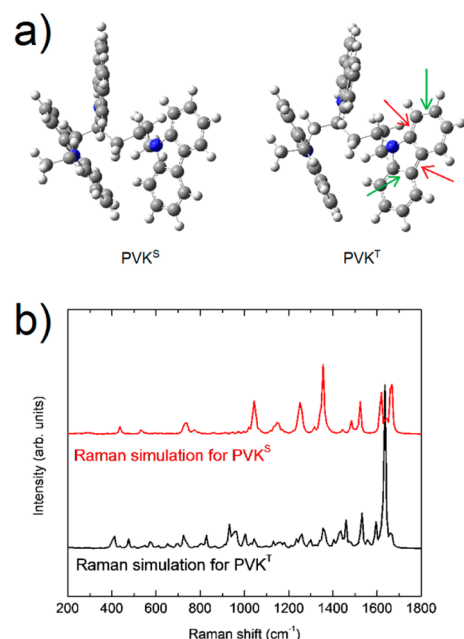


Figure 3. (a) PVK models for singlet-singlet-singlet (PVK^S) and triplet-triplet-triplet (PVK^T) configurations after DFT optimization showing the presence of single and double bonds in PVK^T with green and red arrows, respectively. (b) Theoretical simulation of Raman spectra for both PVK^S and PVK^T configurations.

the increasing amount of TiO_2 quantum dots fractions (x70) showed a slight increase in the intensity of a broad peak at $\lambda \sim 480$ nm. It is important to remark that it is already reported that UV-vis spectra for pure TiO_2 quantum dots dispersion in chloroform only showed absorption below 300 nm, expecting no contribution at higher wavelengths.³³ In our case, there is a redshift to higher wavelengths for $PVK:TiO_2$ -QDs nanocomposites with increasing additions of TiO_2 quantum dots fractions, as previously reported for similar nanocomposites.^{15,34} This redshift observed in the absorption spectra could be possibly due to the formation of bipolaron carbazole species, thus revealing the presence of donor-acceptor electronic interactions.¹⁵ However, the presence of these peaks could be also due to the PVK polaronic bands or also to carbazole species at the interface between PVK and TiO_2 .³⁵ Finally, it is also important to mention that no significant absorption is observed at 532 nm, which is the wavelength of the laser we use to perform our off-resonance Raman spectroscopy analysis discussed in the following sections.

3.3. Raman Results. **3.3.1. Raman Spectroscopy Simulation.** First, we performed the geometrical optimization of PVK oligomers consisting of 3 monomers, after that we proceed to perform vibrational analysis with theoretical Raman spectra calculation. We calculate Raman spectra for the three-monomer oligomers in their singlet-singlet-singlet and triplet-triplet-triplet configurations. PVK models for singlet-singlet-singlet (PVK^S) and triplet-triplet-triplet (PVK^T) configurations after DFT optimization are shown in Figure 3a. All frequencies obtained after calculations were real in both configurations. Raman peak list for PVK singlet and triplet configuration are summarized in Table 1. The theoretical simulation of Raman spectra using both configurations are shown in Figure 3b. The difference between Raman spectra of both configurations differs strongly, as evidenced by the splitting and emergence of several new peaks with low intensity

Table 1. Theoretical and Experimental Raman Frequencies (cm^{-1}) for PVK^S , PVK^T , and $PVK:TiO_2$ -QDs Nanocomposites (x10, x30, x50, x70, x50_0 V and x50_8 V)^a

PVK^S	PVK^T	x10	x30	x50	x70	x50_0 V	x50_8 V
734	724	719	721	723	715	714	715
773	—	761	769	764	750	749	745
—	—	—	—	—	774	—	768
—	—	—	800	804	800	800	795
—	828	—	826	850	840	827	822
—	—	—	—	—	—	—	857
—	—	—	—	876	884	876	888
—	—	910	918	902	916	902	900
—	—	—	—	—	—	—	914
—	931	927	—	927	944	—	927
—	961	944	—	982	966	—	957
—	1004	1016	1018	1019	1013	1009	1014
1044	1044	1049	—	1051	1044	1049	—
—	—	—	1092	1086	1073	1086	1084
1148	1132	1125	1129	1121	1124	1121	1124
—	1160	1157	1158	1161	—	1147	1154
—	1180	1211	1214	—	1208	—	—
—	1236	1229	1221	1234	1230	1221	1216
1252	1259	—	1266	1271	1262	1258	1287
1316	1300	1313	1316	1320	1321	1312	1316
1356	1356	1371	1388	1368	—	1326	1352
—	1403	1403	—	1421	1401	1393	1388
1444	1434	1445	1447	1446	1445	—	1418
1484	1460	1488	1488	1491	1485	1446	1448
1524	—	1522	1527	1528	1512	1479	1476
—	1532	—	—	1552	—	1527	1516
—	1556	1572	1576	1571	1571	1552	1544
—	1597	—	—	1600	1592	1574	1571
1620	—	1622	1624	1624	1620	1590	1589
1642	1636	—	—	—	—	1618	1618
—	—	—	—	—	—	—	1655
1665	1663	—	1667	1672	1676	—	1673
—	—	—	—	1715	1700	—	1699

^aTheoretical Raman frequencies for PVK^S and PVK^T were obtained using DFT calculations (Figure 3). Experimental Raman frequencies for PVK-rich zones of x10, x30, x50 and x70 (Figure 5). Experimental Raman frequencies for PVK-rich zones of x50 with 0 and 8 V applied voltage (Figure 7). All experimental Raman frequencies were collected with ~ 4 cm^{-1} resolution.

for PVK^T configuration in comparison with PVK^S configuration. This is probably in relation with the loss of aromaticity of the triplet configuration respect to the singlet configuration of PVK, as observed in their respective geometries after optimization. Theoretical Raman spectra for PVK^S model showed the presence of vibrational modes at ~ 734 , 773, 1044, 1148, 1252, 1316, 1356, 1444, 1484, 1524, 1620, 1642, and 1665 cm^{-1} , ascribed to PVK out-of-plane benzene ring (C-H) deformation, $\delta(C-C)$ bending, CH_2 rocking, CH_2 twisting, CH_2 wagging, benzene ring $\delta(C-H)$ deformation, tertiary amine ring $\delta(C-H)$ deformation, $\nu(C-N)$, benzene ring $\nu(C=C)$ stretching, and tertiary amine ring $\nu(C=C)$ stretching modes, respectively.³⁶ On the other hand, PVK^T showed the splitting of the previous modes and the appearance of new peaks in the ~ 400 –700, 800–1000, 1150–1250, and 1520–1620 cm^{-1} regions.

3.3.2. Confocal Raman Microscopy. Confocal Raman microscopy images for x10, x30, x50, and x70 nanocomposites are shown in Figure 4. These images were obtained by filtering

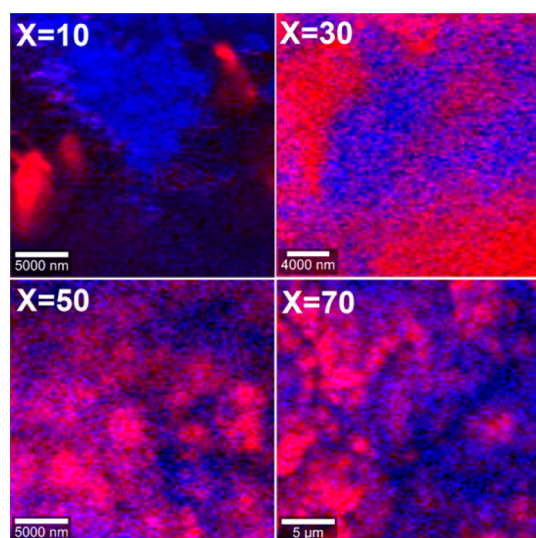


Figure 4. Confocal Raman microscopy images for x10, x30, x50, and x70 nanocomposites obtained by filtering the TiO_2 E_g mode (red) and the PVK $\nu(\text{C}=\text{C})$ mode (blue).

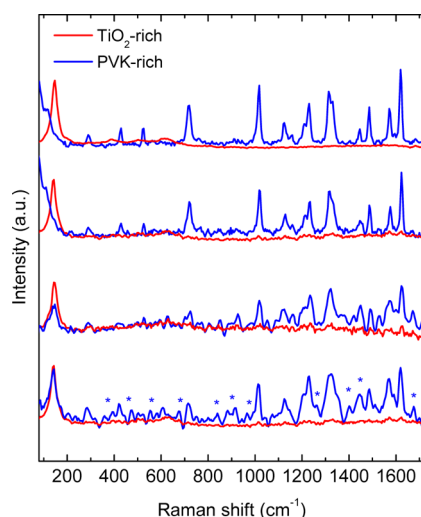


Figure 5. Confocal Raman spectra at selected area for x10, x30, x50 and x70 nanocomposites corresponding to TiO_2 -rich (red) and PVK-rich (blue) zones. Peaks marked with asterisks (*) corresponds to those which are absent in typical PVK Raman spectra.

the TiO_2 E_g mode at 145 cm^{-1} and the PVK $\nu(\text{C}=\text{C})$ mode generating TiO_2 -rich (red) and PVK-rich (blue) zones, respectively. In the case of x50 a major homogeneity in the nanocomposite is observed, while x10 and x30 exhibited some TiO_2 nanoparticles agglomeration. Confocal Raman spectra at selected area corresponding to TiO_2 -rich (red) and PVK-rich (blue) zones are plotted in Figure 5. Raman spectra of TiO_2 -rich zone showed a high intensity and broad peak at $\sim 145\text{ cm}^{-1}$, which is characteristic of the TiO_2 E_g mode of anatase polymorph³⁷ and thus confirming this structural phase for the TiO_2 quantum dots embedded in the PVK host, in agreement with the SAED pattern showed in Figure 1d. Raman spectra of PVK-rich zone, especially for x10 nanocomposite, are associated with typical pure PVK peaks in the singlet configuration, which are summarized in Table 1. PVK Raman peaks situated at $\sim 719, 1016, 1124, 1229, 1316, 1447, 1484, 1571,$ and 1620 cm^{-1} are ascribed to PVK $\delta(\text{C}-\text{C})$ bending,

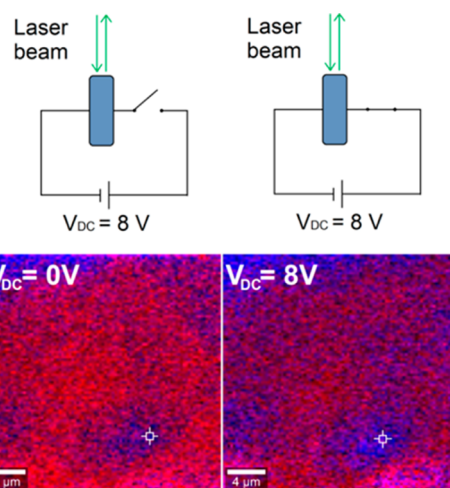


Figure 6. Confocal Raman microscopy images for x50 nanocomposite in the absence ($V_{dc} = 0\text{ V}$) and presence ($V_{dc} = 8\text{ V}$) of applied voltage.

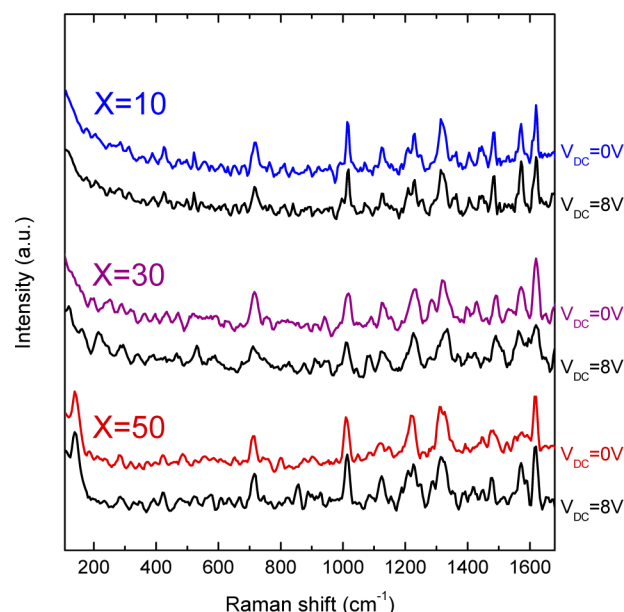


Figure 7. Confocal Raman spectra at selected area for PVK-rich zone of x10, x30 and x50 nanocomposites collected at $V_{dc} = 0$ (color) and 8 V (black) external applied voltage. The selected $\sim 270 \times 270\text{ nm}^2$ PVK-rich area corresponding to the Raman spectra are marked with a white square on each confocal Raman image shown in Figure 6.

CH_2 rocking, CH_2 twisting, CH_2 wagging, benzene ring $\delta(\text{C}-\text{H})$ deformation, tertiary amine ring $\delta(\text{C}-\text{H})$ deformation, $\nu(\text{C}-\text{N})$, benzene ring $\nu(\text{C}=\text{C})$ stretching and tertiary amine ring $\nu(\text{C}=\text{C})$ stretching modes, respectively.³⁶ The increasing concentrations of TiO_2 quantum dots in the nanocomposites, especially for those above x50 concentrations, lead to the appearance of several peaks that cause notorious differences in the Raman spectra. The new low intensity peaks, marked with asterisks in Figure 5, are observed in the $\sim 400\text{--}700, 800\text{--}1000, 1520\text{--}1620\text{ cm}^{-1}$ region, in agreement with those theoretically predicted for PVK in the triplet configuration. However, in order to separate the new experimental peaks observed and attributed to PVK in its triplet configuration, we must consider only those modes observed above 700 cm^{-1} to avoid possible interference of TiO_2 anatase low intensity peaks observed in this region. The appearance of the additional peaks

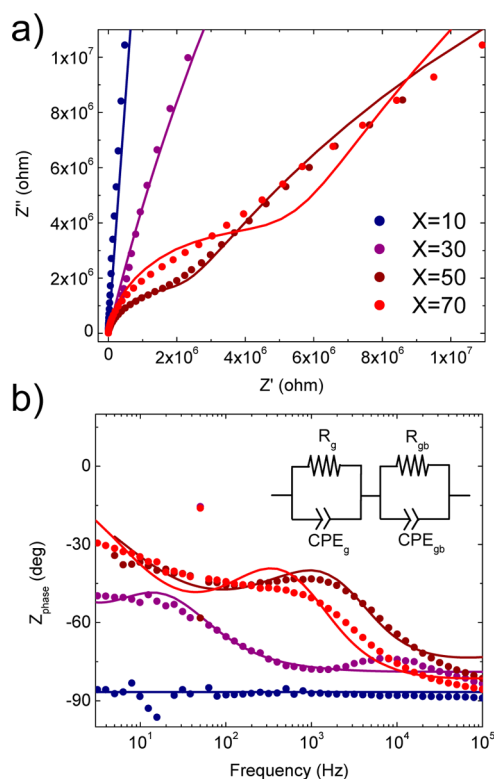


Figure 8. (a) Nyquist plots and (b) phase versus frequency plots at $V_{dc} = 0$ V for x10, x30, x50, and x70 nanocomposites. The circuit model used in the fittings is shown in the inset.

ascribed to the triplet configuration of PVK could be associated with the electronic interaction between the TiO_2 quantum dots and the polymer, leading to a partial modification on the PVK configuration.

3.3.3. Confocal Raman Microscopy with Applied Dc Voltage. Raman spectra for x10, x30 and x50 nanocomposites were collected with and without applied voltage in order to study the effect in the PVK configuration. Confocal Raman microscopy images for x50 in the absence ($V_{dc} = 0$ V) and presence ($V_{dc} = 8$ V) of applied voltage are displayed as an example in Figure 6. These two images were obtained from exactly the same zone in the sample to evaluate only the effect of the absence and presence of an applied voltage in the nanocomposites. The implemented filters to form the confocal Raman image; that is TiO_2 E_g mode and the PVK $\nu(\text{C}=\text{C})$ mode for TiO_2 -rich (red) and PVK-rich (blue) zones, respectively, were also the same for both absence and presence of applied voltage. Confocal Raman spectra at the same selected area collected at $V_{dc} = 0$ and 8 V external applied voltage are shown in Figure 7. No detectable changes were observed

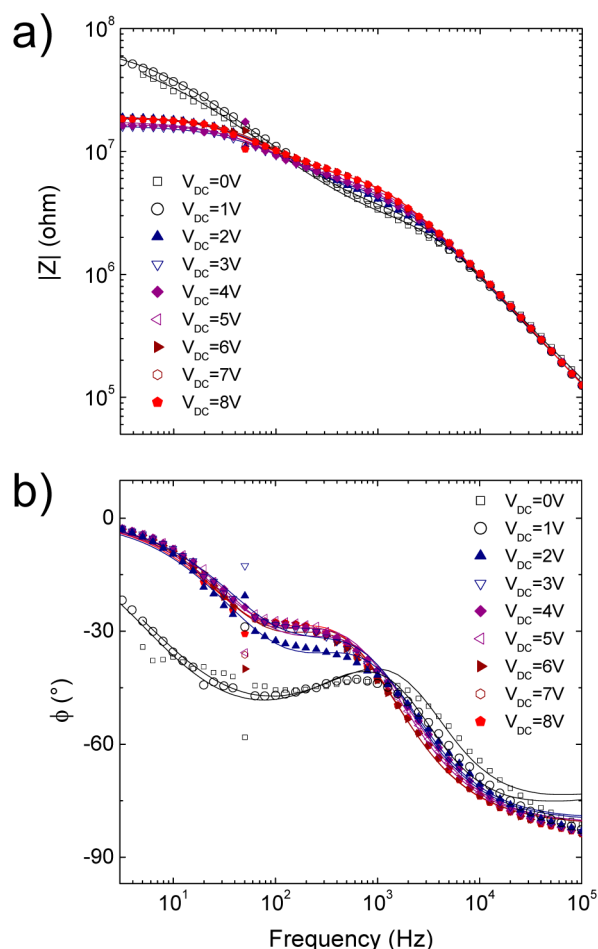


Figure 9. (a) Impedance modulus and (b) phase versus frequency plots at $V_{dc} = 0$ –8 V for x50. All compositions showed the same trend except x10 which exhibited high impedance values avoiding low signal/noise ratio data.

between 0 and 8 V for the particular case of x10 nanocomposite. However, there is an evident modification of Raman spectra of PVK-rich zone with and without applied voltage for x30 and x50, suggested by the occurrence of different peaks and modifications of the relative intensities in the Raman spectra. The most relevant Raman modes modifications for x50 in absence and presence of applied voltage together with theoretical Raman calculations for singlet and triplet configurations are summarized in Table 1. The modifications in the Raman spectra with applied voltage involve the emergence of new peaks, especially for x50 at ~ 930 , 960 , 1420 , and 1660 cm^{-1} that can be associated with the triplet configuration of PVK in agreement with our theoretical Raman calculations. This is suggesting that the increasing population of triplet

Table 2. Impedance Spectra Fitting Analysis for x10, x30, x50, and x70^a

	x10	x30	x50	x70
R_1 (M Ω)	$\sim 10^7$	93 ± 8	1.6 ± 0.1	4.6 ± 0.2
CPE_1 (Q_1 , pF)	14.7 ± 0.1	87 ± 4	36 ± 7	39 ± 3
R_2 (M Ω)	—	1400 ± 60	58 ± 2	74 ± 1
CPE_2 (Q_2 , pF)	—	251 ± 10	1300 ± 700	640 ± 20
σ_T (S cm^{-1})	$\sim 10^{-13}$	6.7×10^{-10}	1.7×10^{-8}	1.2×10^{-8}

^aResistance ($R_{1,2}$) and capacitance ($\text{CPE}_{1,2}$) were calculated from the circuit model fittings shown in Figure 5b-inset. The total conductivity (σ_T) was calculated using $\sigma_T = 1/(\rho_1 + \rho_2)$ using $\rho_{1,2} = R_{1,2}d/A$ with $d = 0.1$ cm as the pellet thickness and $A = 0.1$ cm^2 as the electrode contact area.

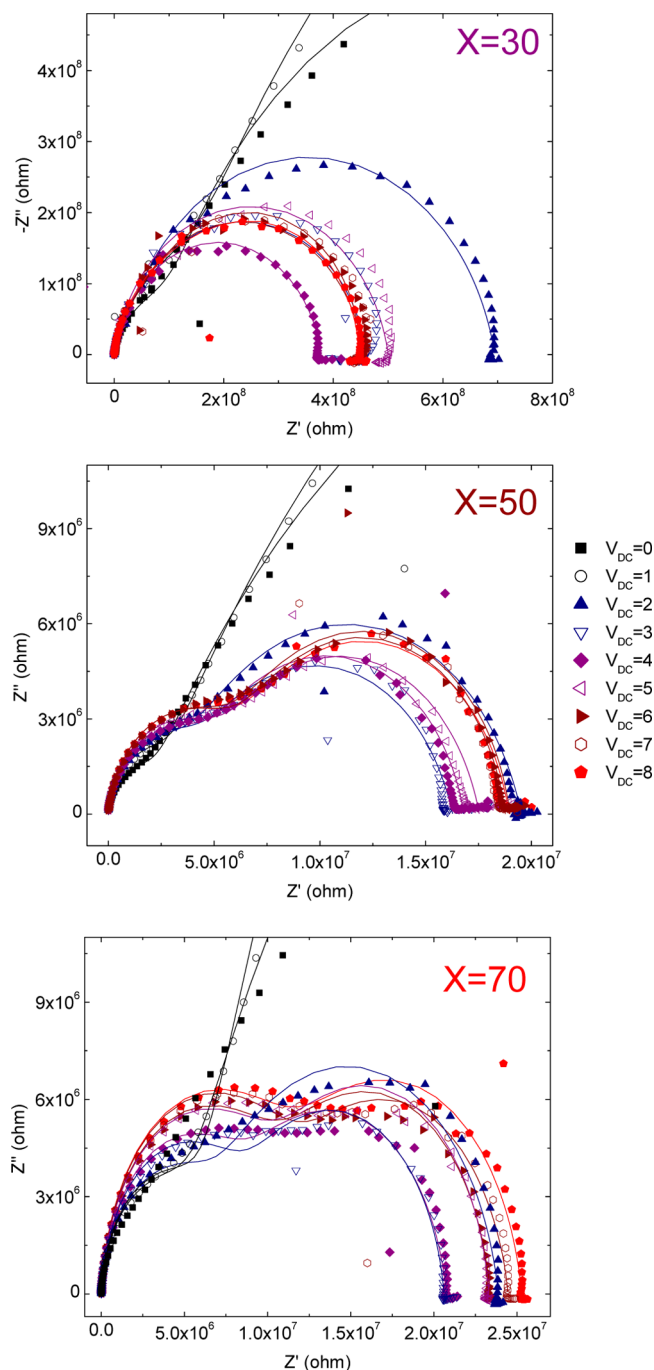


Figure 10. Nyquist plots as a function of different applied dc voltages ranged between $V_{dc} = 0$ and 8 V for selected x30, x50, and x70 nanocomposites.

configuration in PVK polymer is not only observed with increasing TiO_2 quantum dots concentration but also when an external dc voltage is applied. A possible explanation could be based in the charge carrier injection, which leads to a modification of the polymer configuration when the dc voltage is applied.

3.4. Impedance. **3.4.1. Impedance Spectroscopy.** Impedance spectra obtained with 10 mV AC amplitude and zero applied dc bias for x10, x30, x50, and x70 are shown in Figure 8. Nyquist plots represented as imaginary (Z'') versus real impedance (Z') are shown in Figure 8a and phase versus frequency plots are shown in Figure 8b. In all cases, Nyquist

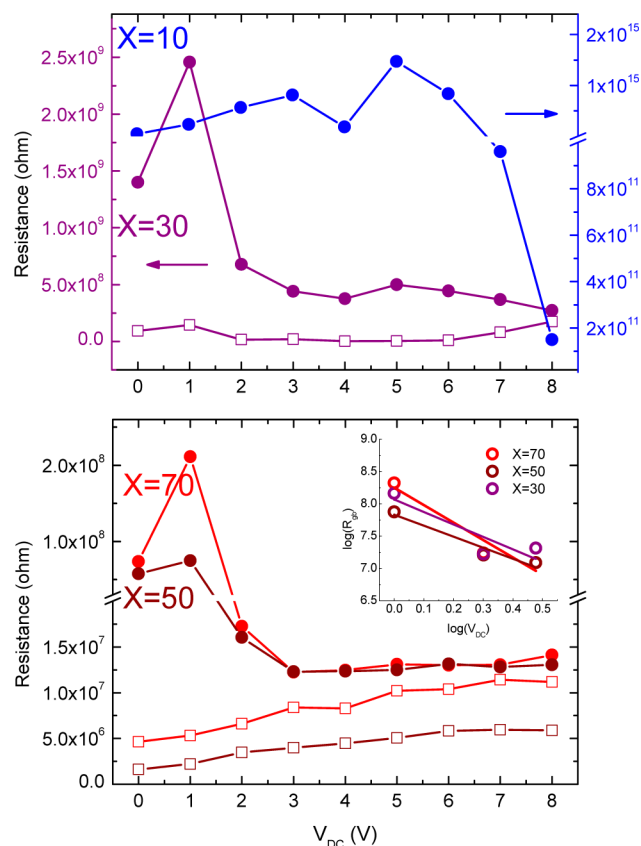


Figure 11. Resistance contributions (R_1 and R_2) dependence with the applied dc voltage marked as empty-squares (R_1) and full-circles (R_2), respectively. The $\log(R_2)$ vs $\log(V_{dc})$ plots for x30, x50, and x70 nanocomposites are shown in the inset.

and phase plots were best fitted with the circuit model shown in Figure 8b inset, characterized by the sum of two contributions of parallel resistance (R) and constant phase element (CPE). The two contributions to the electrical transport can be attributed to different zones in the nanocomposites; one corresponding to a bulk zone ($R_1 - \text{CPE}_1$) and the other to a depletion zone ($R_2 - \text{CPE}_2$) of the polymer nanocomposites, in agreement with previous reports.^{38,39} For the particular case of x10, only a global R –CPE circuit was fitted to describe the large impedance showing resistance values above $\sim 10^{13}$ ohm with associated conductivity of $\sigma \sim 10^{-13}$ S cm^{-1} . These high impedance values are in agreement with the typical low conductivity $\sigma \sim 10^{-14}$ S cm^{-1} observed for pure poly(vinyl carbazole) polymer.⁴⁰ In addition, the Bode plot of phase versus frequency for x10 showed a capacitive behavior ($\phi = -90^\circ$) in the whole frequency regime. However, the presence of higher amounts of TiO_2 quantum dots fillers ($30 < X < 70$) lead to a drastic decrease of several orders of magnitude in the total impedance. The associated total conductivities for $X = 30$, 50, and 70 were 6.7×10^{-10} , 1.7×10^{-8} , and 1.2×10^{-8} S cm^{-1} , respectively. The bode plots of phase versus frequency for x30, x50 and x70 showed a decrease in the phase from $\phi = -90^\circ$ to $\phi = -30^\circ$ values at low frequencies ($f < 10^2$ – 10^3 Hz) suggesting a decrease in the capacitive behavior respect to x10. The above-mentioned observations are suggesting that the presence of TiO_2 quantum dots lead to an increment in the charge carrier mobility in these PVK: TiO_2 –QDs donor:acceptor nanocomposites with optimal performance for x50 composition. However, as we mentioned above, the composi-

tions in the range x30–x70 showed best fit for two contributions of parallel R-CPE elements distinguishing both bulk and depletion zones contributions to the electrical transport. The separate contribution to the resistance (R_1 and R_2) and capacitance (CPE_1 and CPE_2) are summarized in Table 2. For all cases, the $R_1 - CPE_1$ contribution is at least 1 order of magnitude lower than the $R_2 - CPE_2$ contribution. This is suggesting that the $R_2 - CPE_2$ contribution is governing the overall electrical transport and thus the increasing concentration of TiO_2 quantum dots nanofillers leads to an enhancement of the carrier injection process showing the highest mobility for x50 composition.

3.4.2. Impedance Spectroscopy with Applied dc Voltage. The effect of the applied bias on the impedance modulus and phase versus frequency for the x50 composition are shown in Figure 9, parts a and b, respectively. For all cases except x10, a notorious decrease in the impedance modulus of 1 order of magnitude respect to zero bias was observed at low frequencies ($f < 10^2$ Hz) above a $V_{dc} = 2$ V threshold bias. In addition, the phase versus frequency plots showed the same trend, with a transition from capacitive ($\phi \sim -90^\circ$) to resistive ($\phi \sim 0^\circ$) behavior with decreasing frequency. All compositions (x30, x50, and x70) showed the same trend with the exception of x10, for which large impedance values were observed even at very high applied dc voltages ($V_{dc} = 8$ V). It is important to remark that a threshold dc voltage of about 20 V is required for pure PVK to satisfy the condition of moving to a higher mobility configuration.⁴¹ The Nyquist plots for x30, x50, and x70 with different applied dc voltages are shown in Figure 10. It is very clear from these plots that the real impedance drastically decrease above a $V_{dc} = 2$ V threshold voltage showing a minimum value at $V_{dc} = 4$ V for all cases. At higher voltages $V_{dc} > 5$ V the impedance remain in low values but with a slight positive slope with increasing voltage in the $V_{dc} = 5$ –8 V range. The presence of two semicircle arcs in the Nyquist plots was observed for all cases in the whole applied dc voltage range. These two semicircle arcs were associated with bulk and depletion zones contribution to the electrical transport as discussed in the previous section. Large impedance ascribed to the depletion zone contribution was observed for x30 but both contributions tend to equalize for x50 and x70, as evidenced by the similar size of both semicircle arcs shown in Figure 10. The separated R_1 and R_2 contributions to the resistance as a function of the applied dc voltages are displayed in Figure 11. It is clearly observed that $X = 10$ showed high total resistance of $R \sim 10^{14}$ ohm in the $V_{dc} = 0$ –6 V showing a decrease to $R \sim 10^{11}$ ohm when the applied dc exceeded $V_{dc} > 7$ V. On the other hand, $X = 30, 50$, and 70 showed a notorious decrease in the major contribution to the resistance from $R_2 \sim 10^9$ to 10^8 ohm at a $V_{dc} = 2$ V threshold voltage. The rapid decrease of this major contribution to resistance is a clear evidence of the carrier injection process at this applied dc voltage.^{38,39,42} On the basis of the space-charge-limited current (SCLC) theory, a linear dependence is expected for the $\log(R)$ versus $\log(V_{dc})$ plots, with the corresponding slope ($-m$) giving information about the trap distribution of charge carriers.⁴³ The slopes obtained from linear fittings of $\log(R_2)$ versus $\log(V_{dc})$ plots were $m = 1.7, 1.9$, and 2.7 for $X = 30, 50$ and 70 , respectively. This is suggesting that the charge carriers follows the SCLC theory with trap-free space-charge-limited conductivity ($m \sim 2$), as reported recently for other donor:acceptor systems.⁴⁴

4. CONCLUSIONS

In this report, we synthesized poly(vinyl carbazole):titania quantum dots (PVK: TiO_2 -QDs) nanocomposites via water vapor flow diffusion. Confocal Raman and impedance spectroscopy analyses were performed under applied dc voltage evidencing changes in the poly(vinyl carbazole) structure and electrical transport. The structural PVK modifications in the singlet and triplet configurations were correlated with theoretical calculations performing DFT utilizing Gaussian 09 code. The increase of the triplet configuration of poly(vinyl carbazole) was observed with increasing TiO_2 quantum dots concentration and applied dc voltage. These structural modifications were attributed to the electronic interaction and charge injection of PVK: TiO_2 -QDs donor:acceptor system in correlation with impedance spectroscopy analyses. These studies are important to understand the transport mechanism for hybrid donor:acceptor nanocomposites as promising fullerene-free active layer materials for polymer solar cells.

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Notes

The authors declare no competing financial interest.

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