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From positive to negative magnetoresistance behavior at low applied magnetic fields for polyaniline:titania quantum dot nanocomposites

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Here, we report the tuning from the positive to negative magnetoresistance response at room temperature and low applied magnetic fields ($H \sim 200$ mT) for polyaniline nanocomposites prepared via *in situ* growth of titanium oxide quantum dots. In addition, we showed experimental Raman evidence revealing that the positive magnetoresistance response in these polyaniline nanocomposites is mediated by the bipolaron mechanism. Confocal Raman spectroscopy under applied magnetic field analysis showed the decrease of the polaron population to form bipolarons of polyaniline when exposed to an applied magnetic field for the TiO_2 quantum dot diluted regime. Negative magnetoresistance, observed for the TiO_2 quantum dot higher concentration regime, was attributed to the suppression of polyaniline polarons probably associated with its partial chemical functionalization at the interface due to the increasing concentration of TiO_2 quantum dots. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4989831>]

I. INTRODUCTION

The discovery of organic magnetoresistance (OMAR) has brought broad interest in the development of novel spintronic materials with light weight, high flexibility, and low cost.^{1–5} These materials could have promising applications as sensors for intelligent areas^{6–9} and lightening LED devices.¹⁰ The OMAR effect has been observed in a lot of conductive polymers but one of the most promising is polyaniline due to its easy preparation, low cost, and broad versatility for different sensing applications.^{11–13} However, the OMAR response of pure polyaniline is generally observed at low temperatures and large magnetic fields are necessary to achieve high OMAR values.^{14,15} The transition from negative to positive magnetoresistance (MR) has been observed for polyaniline nanofibers at $T \sim 90$ and 100 K, as previously reported by Bozdogan *et al.*¹⁴ and Nath *et al.*,¹⁵ respectively. Both negative and positive magnetoresistance values have been reported for polyaniline and other polymer nanocomposites at low and high temperatures, respectively.^{14–18} Nevertheless, there are also recent reports showing transition from positive to negative magnetoresistance behavior at room temperature for polyaniline coated carbon fabrics composites.¹⁹ In order to explain this behavior, one of the most accepted mechanisms is the forward interference²⁰ and shrinkage of electronic wave-function²¹ models for negative and positive magnetoresistance (MR), respectively. Nevertheless, there are other interpretations to the positive and negative OMAR response for polyaniline based in the bipolaron model first presented by Bobbert *et al.*²² Recently, the preparation of polyaniline nanocomposites with silicon²³ and silica²⁴ additions has been reported showing an enhancement on the positive OMAR response at room temperature. However, the

transition from positive to negative magnetoresistance was observed at room temperature when a sufficiently high magnetic field is applied, i.e., $H \sim 5$ T. This is evidencing that a difference in the preparation of polyaniline nanocomposites could lead to a giant positive OMAR response at room temperature. On the other hand, polyaniline nanocomposites prepared with titania additions have recently been reported showing giant negative magnetoresistance at $H \sim 8$ T at room temperature.²⁵ However, there is still interest in the organic magnetoresistance response at lower applied magnetic fields which could have potential interest for technological application purposes. In addition, there is still no conclusive information about the mechanism of the OMAR effect at low applied magnetic fields. Due to these reasons, in this report, we show the *in situ* growth of titanium oxide quantum dots into the polyaniline host (PANI- TiO_2 -X) and its effect on the transition from the positive to negative magnetoresistance response at low applied magnetic fields.

II. MATERIALS AND METHODS

Polyaniline (PANI-DBSA- H_2SO_4) in its emeraldine salt form 99.9% with average $M_w \sim 15000$ and titanium tetrapropoxide (TTP) 98% were purchased from Sigma-Aldrich. 0.3 g of PANI was suspended in 20 ml of tetrahydrofuran (THF) and 1 ml of deionized water (H_2O) under stirring at 500 rpm for approximately 30 min. The corresponding amount of TTP was added to the PANI suspension and kept stirring at $T = 343$ K until dryness. The emerging dark green powder was ground and exposed to deionized water vapor at $T = 353$ K with a vapor flow of ~ 1 ml/min during 10 h. All compositions were finally dried at $T = 353$ K under vacuum for 7 h to eliminate propanol generated from the hydrolysis process and the residual water. The PANI- TiO_2 dried powder was then ground and compressed at 50 kN/cm^2 pressure to form pellets. The nanocomposites studied in this report were

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named as PANI-TiO₂-X with X=20, 30, 40, 50, and 60, with X corresponding to the weight fraction of TiO₂, respectively.

The morphology and particle size of the PANI-TiO₂-X nanocomposites were characterized by high-resolution transmission electron microscopy (HR-TEM) using a JEOL 2100 instrument working under a 200 kV voltage. Small-angle X-ray scattering (SAXS) was performed at SAXS-1 Beamline Station as implemented at Laboratório Nacional de Luz Síncrotron (LNLS-CNPEM) in Campinas (Brazil), working with 8 keV radiation in the $q=0.1\text{--}4.0\text{ nm}^{-1}$ range at $T=273\text{--}373\text{ K}$. PANI-TiO₂-X nanocomposites were studied by confocal Raman microscopy obtained using WITec Alpha 300-RA equipment. Raman spectra were additionally collected with and without low applied magnetic field (H), using a device where the sample pellet is located between two parallel permanent neodymium magnets. The magnets were located parallel to the laser beam and the separation between the magnets was $\sim 0.80\text{ mm}$, enabling a magnetic field of $H \sim 200\text{ mT}$, measured with a gaussmeter. Raman spectra for the PANI-TiO₂-40 nanocomposite were collected using an excitation wavelength of 532 nm laser wavelength and the laser power was adjusted to $\sim 3\text{ mW}$ to avoid polyaniline decomposition. 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. DC conductivity versus temperature measurements were obtained using the four-probe technique in the temperature range $T=12\text{--}324\text{ K}$ using a Janis CCS-150 cryogenic system. Magnetoresistance (MR) measurements were obtained using the applied magnetic field (H) range $0 < H < 350\text{ mT}$ and calculated as $\text{MR}(\%) = 100 * [R(H) - R(H=0)]/R(H=0)$.

III. RESULTS AND DISCUSSION

The high-resolution transmission electron microscopy (HRTEM) images of PANI-TiO₂-X for the particular case of X=40% are shown in Fig. 1. The low magnification HRTEM image showed that the *in situ* growth of TiO₂ quantum dots into the polyaniline matrix lead to a homogeneous nanocomposite, as we previously reported.²⁶ The high

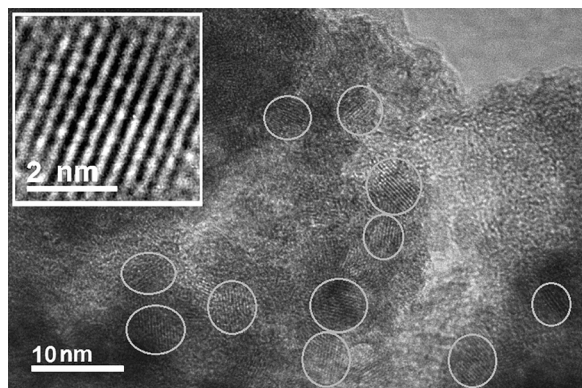


FIG. 1. HRTEM images in low magnification and high magnification (inset) for PANI-TiO₂-X with X=40. The circles are a guide to the eye to show the TiO₂ quantum dots embedded in the polymer host.

magnification HRTEM image shown in the Fig. 1-inset revealed the presence of quasi-spherical TiO₂ quantum dots with a $\sim 5\text{ nm}$ diameter. The inter-planar spacing (d) estimated from the Fourier transform pattern was $d \sim 3.5\text{ }\text{\AA}$, in possible agreement with the (101) plane for TiO₂ in its anatase polymorph.²⁶ Further discussion on the characterization of the TiO₂ quantum dot structure and size for the same PANI-TiO₂-X nanocomposites estimated by means of high-resolution transmission electron microscopy, X-ray diffraction, Raman, and small angle X-ray scattering can be found in our previous report.²⁶ In the present report, we show additional small angle X-ray scattering (SAXS) analysis, performed in transmission geometry at different temperatures. It is important to study any possible microstructural modification with temperature to discard additional contributions, other than temperature itself, which could influence the electrical transport mechanism. In this case, the results verify no drastic changes in the microstructure of the system in the range of $T=273\text{--}373\text{ K}$, as shown in Fig. 2. Effectively, no drastic variations in the polyaniline mean correlation length or TiO₂ quantum dots mean particle size was observed for a given composition at different temperatures. The mean correlation length (d) observed for polyaniline evidenced as a relative maximum at $q_{\text{max}} \sim 2\text{ nm}^{-1}$ in the SAXS curves associated with $d \sim 2\pi/q_{\text{max}} \sim 3\text{ nm}$ could be in possible relation to the mean polyaniline interfiber separation distance. This correlation length is progressively vanished with increasing TiO₂ quantum dot concentration, suggesting that they are possibly occupying the empty spaces between polyaniline fibers. The mean quantum dot size (D) for all TiO₂ quantum dot compositions, estimated using the Beaucage

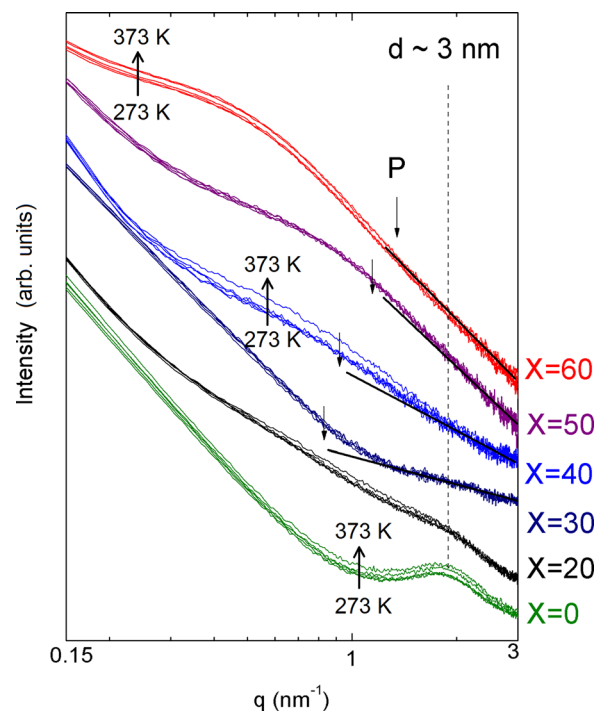


FIG. 2. SAXS curves for PANI-TiO₂-X with X=0, 10, 20, 30, 40, 50, and 60 in the temperature regime $T=273\text{--}373\text{ K}$. The correlation length (d) ascribed to the polyaniline interfiber mean separation distance and the Porod exponent (P) extracted from the slope are marked as a guide to the eye.

equation,²⁷ was $D \sim 3\text{--}8\text{ nm}$ in the whole temperature regime. However, the increase in the quantum dot concentration from $X = 30$ to $X = 60$ showed an increase in the Porod exponent from $P \sim 1$ to $P \sim 2$ establishing a possible transition from quasi-2D and 3D fractal dimensionality, as previously reported.²⁶

Raman spectra of PANI-TiO₂-X nanocomposites are shown in Fig. 3. Raman spectra confirmed the presence of TiO₂ quantum dots, associated with characteristic bands at $\sim 153\text{ cm}^{-1}$ and other lower intensity peaks at 415, 515, and 630 cm^{-1} , ascribed to E_g , B_{1g} , A_{1g} , and E_g modes of TiO₂ anatase polymorph, respectively.²⁸ On the other hand, the presence of polyaniline was evidenced by the presence of peaks at ~ 576 , 830, 1170–1250, 1334, 1415, 1486, 1590, and 1620 cm^{-1} ascribed to C-N-C-H out-of-plane deformation, C-H wagging, C-H bending, polaron C-N⁺ stretching, C-N stretching, C=N stretching, C-C stretching, and C=C stretching modes, respectively.²⁶ An increase in the peak intensity ascribed to the polaron C-N⁺ stretching mode at 1334 cm^{-1} was observed for $X = 20\text{--}40$, while a decrease in the polaron band was observed for $X = 50\text{--}60$. Based on experimental and theoretical Raman studies, we have already reported that both polaron and bipolaron configurations of polyaniline showed a distinctive vibrational signature in the Raman spectra.^{26,29} The presence of the peak at $\sim 1334\text{ cm}^{-1}$ showed a drastic decrease in its relative intensity in the bipolaron configuration.²⁹ In the present case, the increase in the relative intensity of the $\sim 1334\text{ cm}^{-1}$ peak due to the addition of low amounts of TiO₂ quantum dots ($X < 40$) could be suggesting an increase in the polaron population. However, at higher TiO₂ concentrations

($X > 40$) there is a slight decrease in the relative intensity of the polaron band at $\sim 1334\text{ cm}^{-1}$ and an increase in relative intensity of a peak at $\sim 1500\text{ cm}^{-1}$, which could be associated with the partial chemical functionalization of polyaniline at the TiO₂ quantum dot interface, as previously reported.²⁶ In addition, we showed the effect of a low applied magnetic field ($H = 200\text{ mT}$) on the Raman spectra of PANI-TiO₂-X nanocomposites in order to observe possible modifications in the polyaniline polaron configuration. For this reason, we performed Raman analysis using a device consisting of two parallel permanent magnets separated by the sample pellet, as schematized in Fig. 4(a). Confocal Raman microscopy images with $(25 \times 25)\text{ }\mu\text{m}^2$ total area with a grid of (90×90) points are shown using ~ 9000 Raman spectra. The confocal Raman microscopy images shown in Fig. 4(b) were obtained by filtering the TiO₂ anatase E_g mode at $\sim 153\text{ cm}^{-1}$ and polyaniline C=C stretching mode at $\sim 1620\text{ cm}^{-1}$ in relation to TiO₂-rich (red) and PANI-rich (blue) zones, respectively. Both confocal Raman

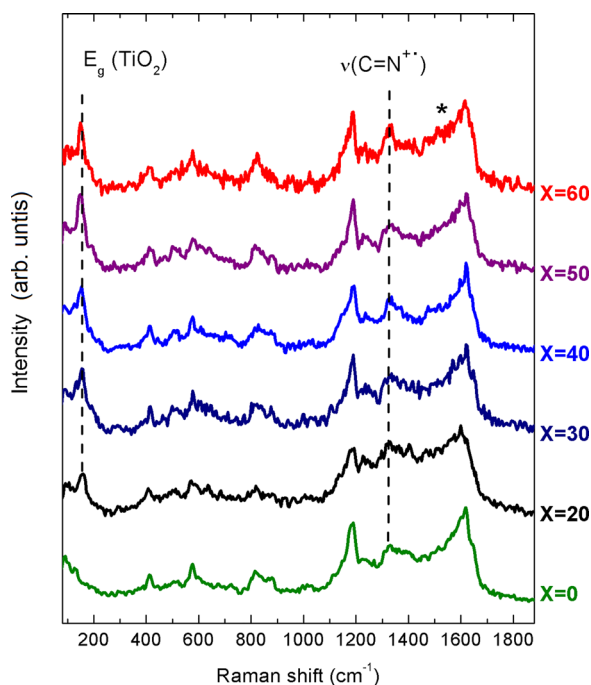


FIG. 3. Raman spectra of PANI-TiO₂-X nanocomposites with $X = 0, 20, 30, 40, 50$, and 60 . The anatase TiO₂ E_g mode and polyaniline polaron (C=N⁺) stretching mode are marked as references. The shoulder peak marked with an asterisk (*) was assigned to (C=N) stretching mode with C=N $\sim$ Ti-O chemical interaction.

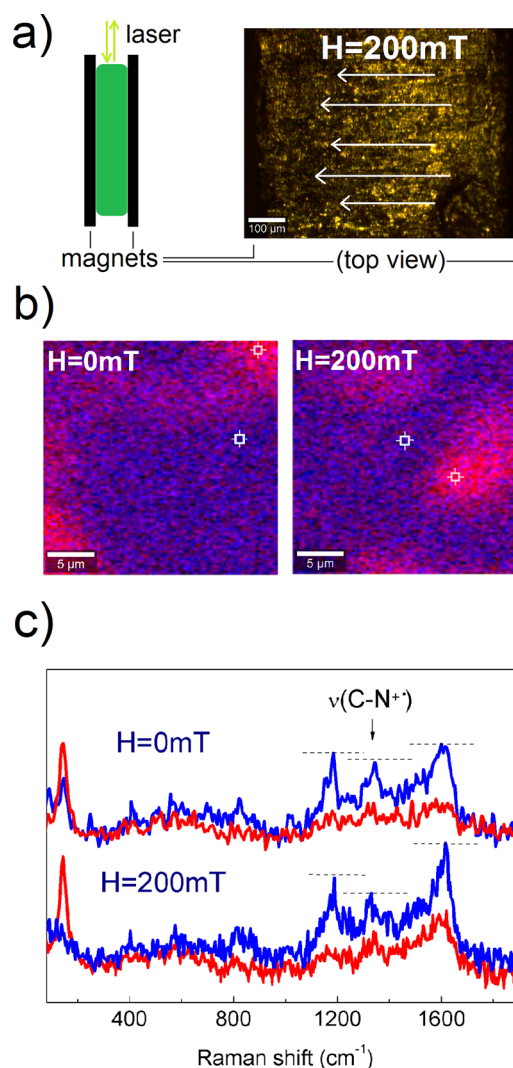


FIG. 4. (a) Scheme and top view optical images of the configuration device for confocal Raman microscopy under applied magnetic field. (b) Confocal Raman microscopy images and (c) confocal Raman spectra corresponding to PANI-TiO₂-40 without ($H = 0\text{ mT}$) and with ($H = 200\text{ mT}$) applied magnetic field. The Raman spectra correspond to the TiO₂-rich (red) and PANI-rich (blue) zone marked in the confocal Raman microscopy images.

images collected with ($H = 200$ mT) and without ($H = 0$ mT) applied magnetic field shown in Fig. 4(b) correspond practically to the same zone of the PANI-TiO₂-X = 40 sample. However, in order to have an adequate qualitative comparison between absence and presence of magnetic field, we focused in the Raman spectra corresponding to well-defined regions of the TiO₂-rich and PANI-rich zones. These Raman spectra for selected zones at $H = 0$ and 200 mT magnetic field are shown in Fig. 4(c), revealing the decrease in the relative intensity of the polaron mode at ~ 1334 cm⁻¹ when the $H = 200$ mT magnetic field is applied. This is suggesting that the presence of this low applied magnetic field favors the transition from polaron to the bipolaron configuration for the polyaniline polymer when loaded with a certain concentration of TiO₂ quantum dots ($X = 40$).

Resistivity versus temperature curves for PANI-TiO₂-X nanocomposites are shown in Fig. 5. All curves showed an exponential increase of resistivity with decreasing temperature, in agreement with a typical semiconductor behavior. PANI-TiO₂-X with $X = 20$ –40 showed a decrease in the resistivity and $X = 50$ –60 showed an increase in the resistivity, all in comparison to pure PANI. The electrical transport in the higher temperature regime ($T \sim 255$ –300 K) can be described using the Arrhenius law, with the following dependence:

$$\sigma(T) \approx \exp\left(-\frac{E_a}{k_B T}\right) \quad T > 255 \text{ K},$$

where E_a is the activation energy, k_B is the Boltzmann constant, and σ is the dc conductivity. Arrhenius plots with linear dependence $\ln(\sigma)$ vs T^{-1} for PANI-TiO₂-X are shown

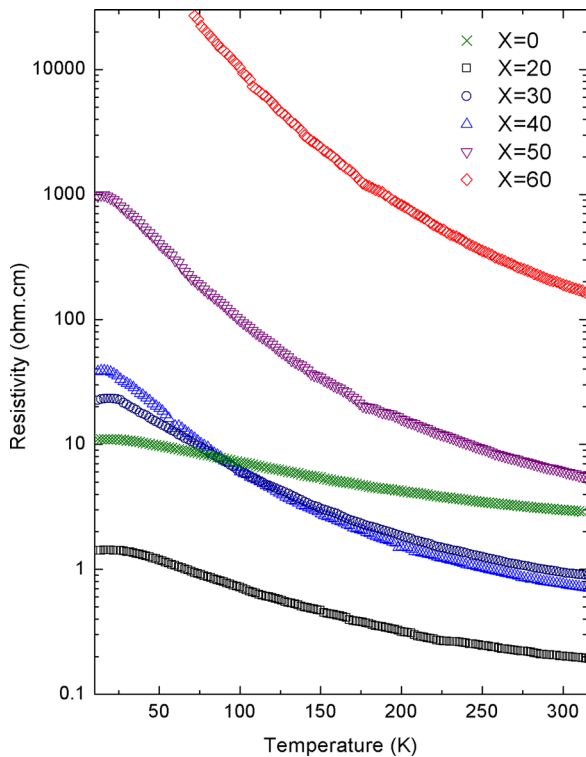


FIG. 5. Resistivity versus temperature plots for PANI-TiO₂-X with $X = 0, 20, 30, 40, 50$, and 60 in the $T = 15$ –325 K temperature regime.

in Fig. 6(a). In all measurements, the linear fit showed no significant deviation from linearity in the $T > 255$ K temperature regime. The activation energy ($E_{a,0}$) obtained from the linear fit of $\ln(\sigma)$ vs T^{-1} plots is $E_{a,0} \sim 25$ meV, 34 meV, 38 meV, 54 meV, and 79 meV for $X = 20, 30, 40, 50$, and 60 , respectively. An increase in the activation energy is observed with increasing TiO₂ concentration as expected due to its poor electrical transport. At lower temperatures, Arrhenius plots show a deviation from linearity; this behavior could be described by the model proposed by Larkin and Khmel'nitskii, based on a logarithmic dependence of the activation energy for disordered systems with a large localization length. Based on this model, the localization length (L_c) should be equal to the length of the hop (x_0) at the transition temperature $T \sim 255$ K and x_0 increases in relation to L_c with decreasing temperatures, as it can be seen in the following equation:

$$\sigma(T) \approx \exp\left(-\frac{T_1[\ln(\alpha T - \beta)]}{k_B T}\right) \quad 70 \text{ K} < T < 255 \text{ K},$$

with α and β depending on the localization length, electric field, hopping length, and pellet thickness.³⁰ All cases showed excellent fits using the activation energy logarithmic dependence with temperature for the $T \sim 255$ –70 K regime as shown in Fig. 6(a). The T_1 parameter related to activation energy logarithmic dependence was $T_1 \sim 0.840$ eV, 1.516 eV, 1.828 eV, 2.583 eV, and 3.048 eV for $X = 20, 30, 40, 50$, and 60 , respectively, suggesting that the length of hopping is affected by the presence of TiO₂ in the low temperature regime.

The reduced activation energy (W) is defined by the following equation:

$$W \approx \left(\frac{\partial \ln \sigma}{\partial \ln T}\right).$$

We plot $\log W$ versus $\log T$ as represented in Fig. 6(b), in order to obtain the electric transport dimensionality (n) which is extracted from the slope (ν) using $\nu = 1/(1 + n)$.³¹ The electrical transport dimensionality is $n \sim 2.0, 2.7, 2.9, 3.1$, and 3.2 for $X = 20, 30, 40, 50$, and 60 , respectively, suggesting an increment in the dimensionality of the hopping process with TiO₂ additions, increasing from quasi-2D to quasi-3D. It is important to remark that the electrical transport dimensionality is in excellent agreement with the dimensionality obtained by SAXS analyses, as discussed above. In both cases, there is strong evidence of transition from quasi-2D to quasi-3D for structural and electrical dimensionalities with increasing TiO₂ quantum dot concentration from $X = 0$ to 60 .

Magnetoresistance (MR) versus applied magnetic field (H) curves obtained at room temperature for PANI-TiO₂-X nanocomposites are shown in Fig. 7(a). A zero magnetoresistance response was observed at room temperature for pure polyaniline and a polyaniline nanocomposite with the lowest amounts of TiO₂ quantum dot weight fractions ($X = 20$). However, an increase in the positive magnetoresistance response was observed for TiO₂ quantum dot weight fraction

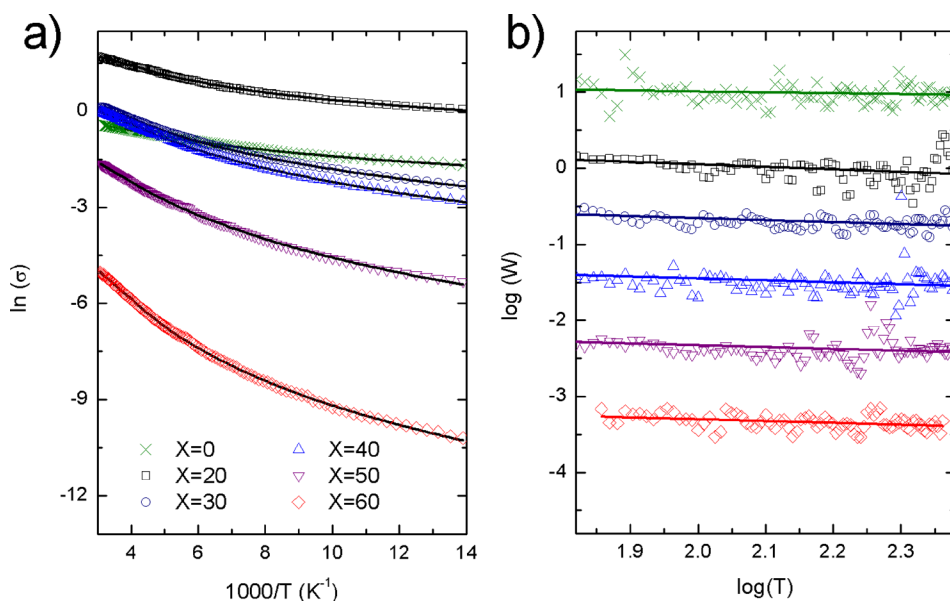


FIG. 6. (a) Arrhenius and (b) Reduced activation energy plots for PANI-TiO₂-X with X = 0, 20, 30, 40, 50, and 60 in the T = 15–325 K temperature regime.

higher than X = 30 showing maximum positive magnetoresistance $MR_{\max} \sim +0.6$ and $+1.0\%$ for X = 30 and 40, respectively, as shown in Fig. 7(b). Based on our previous analysis using confocal Raman microscopy, we evidenced the partial transition from the polaron to bipolaron configuration of polyaniline when an $H = 200$ mT magnetic field is applied. For this reason, we fit the MR vs H curve following the bipolaron model. The MR dependence with H in the bipolaron model can be expressed as follows:

$$MR(H) \approx \frac{H^2}{(H_0^2 + H^2)}.$$

The Lorentzian line shape dependence of MR versus H, first predicted by Bobbert *et al.*,²² has been experimentally observed at room temperature under low applied magnetic fields for other organic semiconductors.^{15,32,33} Briefly, the bipolaron model is frequently used to explain the positive magnetoresistance response based on the formation of bipolarons at the expense of polarons when a low magnetic field

is applied in organic semiconductors.²² This positive magnetoresistance response is in full agreement with the decrease in polyaniline polarons to form bipolarons predicted by our characterization using confocal Raman spectroscopy in the absence and presence of an applied magnetic field. On the other hand, the appearance of a negative magnetoresistance contribution was observed at higher magnetic fields ($H \sim 150$ – 250 mT) with increasing TiO₂ quantum dot concentration in the X > 40 regime. This negative contribution to the total magnetoresistance leads to a transition from the positive to negative magnetoresistance response at room temperature using low applied magnetic fields. The positive to negative magnetoresistance crossover is shown in Fig. 7(a) at applied magnetic field values $H \sim 180$ and 280 mT for X = 50 and 60, respectively. PANI-TiO₂-X with X = 60 showed the highest negative magnetoresistance response, i.e., $MR_{\max} = -0.6\%$ at $H = 350$ mT, as shown in Fig. 7(b). In order to explain the negative contribution to the OMAR response for the TiO₂ concentrated regime, the bipolaron model could

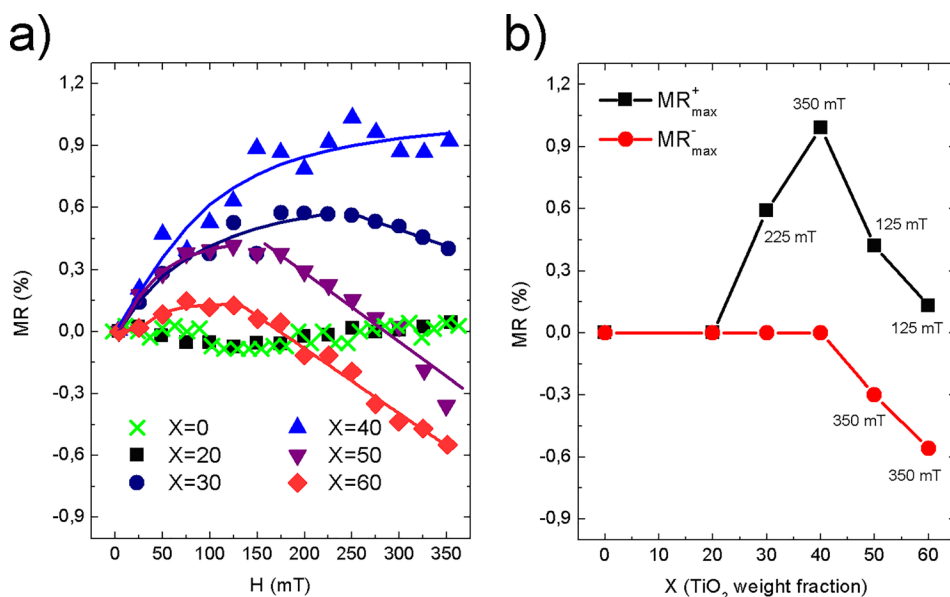


FIG. 7. (a) Magnetoresistance versus applied field and (b) maximum positive and negative magnetoresistance modulus versus TiO₂ quantum dot weight fraction at T = 295 K for PANI-TiO₂-X with X = 0, 20, 30, 40, 50, and 60. The magnetic field at which the maximum magnetoresistance was observed is marked for each case.

also be the first option to consider. The presence of highly concentrated TiO₂ quantum dots in the presence of an applied magnetic field could be favoring the increment of the long-range Coulomb repulsion leading to an increase in the polaron population at the expense of bipolarons. However, the Lorentzian dependence of the MR versus H for the bipolaron model should exhibit a trend to a MR saturation value at high magnetic fields. In our case, no Lorentzian contribution to the negative magnetoresistance could explain the transition from positive to negative contribution observed at $H > 150$ mT for $X > 40$. The negative magnetoresistance in the TiO₂ concentrated regime could have its origin in the irreversible partial suppression of polarons in polyaniline due to chemical functionalization with the increasing amount of TiO₂ quantum dots, as suggested in the Raman analyses discussed above. The declining of the polyaniline polaron population is also in correlation with the drastic decrease in the electrical conductivity observed for $X = 50$ and 60 in the absence of any external magnetic field. In addition, the transition from quasi-2D to quasi-3D electrical transport dimensionality for the TiO₂ concentrated regime ($X > 40$) is also suggesting that the hopping process is drastically modified with respect to the TiO₂ diluted regime ($X < 40$). Moreover, the negative magnetoresistance contribution showed excellent fit with a linear MR versus H dependence, as also observed for other conductive polymer nanocomposites.^{23–25,34–36} The linear dependence of negative magnetoresistance with the applied magnetic field for high TiO₂ concentration nanocomposites could be explained based on the forward interference model using the following equation:

$$MR(H) \approx -C_{sat} \frac{H}{H_{sat}},$$

where C_{sat} is the temperature independent magnetoresistance at the effective saturation magnetic field (H_{sat}). The forward interference model could be explained based on the increase of the resistivity by the quantum interference of different current pathways which lead to an enhancement in the conductivity when a magnetic field is applied. In our case, the increase in the TiO₂ quantum dot concentration and the irreversible partial suppression of the polyaniline polaron population due to chemical functionalization at the interface are probably causing interference to the electrical transport in the absence of the applied magnetic field. In this scenario, an increase in the electrical transport is expected when the magnetic field is applied, thus leading to negative magnetoresistance as it was observed for the nanocomposites with a higher concentration of TiO₂ quantum dots.

IV. CONCLUSIONS

We report the study of the transition from the positive to negative magnetoresistance response at low applied magnetic fields for polyaniline nanocomposites prepared via *in situ* growth TiO₂ quantum dots. We observed an increase in the activation energy with TiO₂ additions and an increment in the electrical transport dimensionality from quasi-2D to quasi-3D, in agreement with SAXS analyses. Magnetoresistance (MR) versus low applied magnetic field (H) curves obtained

at room temperature showed a transition from positive to negative values with increasing TiO₂ quantum dot concentration from $X = 0$ to 60 . We observed the maximum positive MR value at room temperature for $X = 40$, i.e., $MR \sim 1.0\%$ at 350 mT. This positive magnetoresistance response was explained by the bipolaron mechanism and also supported by using confocal Raman spectroscopy in the absence and presence of an applied magnetic field. The presence of an applied magnetic field ($H = 200$ mT) leads to a decrease in the relative intensity of the polaron Raman mode suggesting a transition from polaron to bipolaron configuration, in agreement with the bipolaron model used to explain the positive magnetoresistance response. On the other hand, the highly TiO₂ concentrated regime ($X = 60$) showed the maximum negative MR value, i.e., $MR \sim -0.6\%$ at 350 mT, probably associated with the irreversible suppression of polarons due to chemical functionalization of polyaniline at the TiO₂ interface. The tuning and understanding of the magnetoresistance response at low applied magnetic fields shown in this report could be of great relevance for novel electronic device applications.

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