The effect of TiO$_2$ nanocrystal shape on the electrical properties of poly(styrene-$b$-methyl methacrylate) block copolymer based nanocomposites for solar cell application

Laida Cano$^a$, Junkal Gutierrez$^a$, A. Evelyn Di Mauro$^b$, M. Lucia Curri$^b$, Agnieszka Tercjak$^{a,*}$

$^a$ Group ‘Materials + Technologies’, Chemical Engineering and Environmental Department, Polytechnic School, University of the Basque Country (UPV/EHU), Pza. Europa 1, 20018 Donostia-San Sebastián, Spain

$^b$ CNR-IPCF-Bari Division, c/o Chemistry Department, University of Bari, Via Orabona 4, 70126 Bari, Italy

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Titanium dioxide (TiO$_2$) nanocrystals were synthesized into two shapes, namely spherical and rod-like and used for the fabrication of polystyrene-block-poly(methyl methacrylate) (PSMA) block copolymer based nanocomposites, which were employed as the active top layer of electro-devices for solar cell application. Electro-devices were designed using nanocomposites with high TiO$_2$ nanocrystal contents (50-70 wt%) and for comparison as-synthesized TiO$_2$ nanospheres (TiO$_2$NSs) and TiO$_2$ nanorods (TiO$_2$NRs) were also used. The morphology of the electro-devices was studied by atomic force microscopy showing good nanocrystal dispersion. The electrical properties of the devices were investigated by PeakForce tunneling atomic force microscopy and Keithley semiconductor analyzer, which showed higher electrical current values for devices containing TiO$_2$NRs in comparison to TiO$_2$NSs. Remarkably, the influence of the PSMA block copolymer on the improvement of the conductivity of the electro-devices was also assessed, demonstrating that the self-assembling ability of block copolymer can be beneficial to improve charge transfer in the fabricated electro-devices, thus representing relevant systems to be potentially developed for photovoltaic applications. Moreover, the absorbance of the prepared electro-devices in solar irradiation range was confirmed by UV–vis spectroscopy characterization.

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1. Introduction

Organic photovoltaic devices are an attractive alternative to achieve a low cost, light weight and environmentally friendly solar energy source [1–5]. Organic solar cells based on polymers, in particular, have been widely investigated owing to their ease of fabrication in comparison to conventional solar cell devices. However, the main drawback of polymer based photovoltaic devices is their lower solar power efficiencies generally up to 10% [3,5,6] as a consequence of the absence of components with high electron mobility. Consequently, this point is being extensively studied in order to achieve organic photovoltaic devices with higher carrier transport. One of the ways to enhance the charge transfer in an organic solar cell is the combination of polymers with inorganic semiconductors, resulting in hybrid inorganic/organic optoelectronic devices, such as photovoltaic systems [3,7,8]. Among the different inorganic semiconductors, TiO$_2$ inorganic nanocrystals (NCs) are frequently used as semiconductor in solar cell devices [3,4,7–14] since they deliver the highest energy conversion efficiency comparing to other available semiconductors. However, semiconductive inorganic NCs can also strengthen the optical properties of polymers in the energy conversion device, especially for photovoltaic applications, since that can extend the overall absorption range. In this perspective, the synthetic protocol for the fabrication of TiO$_2$NCs is particularly crucial, as it is required to enable a suitable control on the NC size, shape and surface properties, all characteristics that strongly affect the nanomaterial efficiency as active components of solar energy conversion systems. In addition, the device performances are strongly dependent on the hybrid active layer morphology on the nanometer scale.

Many research works have focused on nanostructured composites and hybrid layers, which are viable for a variety of technological applications, including energy conversion in organic solar cells [8,15,16]. In our previous work, nanostructured hybrid composites were developed, by using poly(styrene-$b$-methyl
methacrylate) (PSMMA) block copolymer as a template for the dispersion of as-synthesized colloidal TiO₂ nanorods (TiO₂NRs), which were incorporated into the polymer matrix up to high contents resulting in conductive nanocomposites [17]. In this work, the objective is to characterize novel electro-devices fabricated with a layer of TiO₂–PSMMA nanocomposite as a first approach to consider their potential application in optoelectronic devices. The synthesis of TiO₂ NCs has been carried out by two different colloidal routes based on the hydrolysis of titanium tetraisopropoxide in oleic acid as surfactant, which gave the possibility to manipulate the NC growth kinetics and achieve size and shape control over resulting NCs. Thus, this allowed to obtain NCs with different size and shape depending on the synthesis protocol and to investigate the influence of the NC size and shape on the characterization of electro-devices based on nanocomposites.

The two kinds of as-synthesized TiO₂ NCs employed in this work, TiO₂ nanospheres (TiO₂NSs) and nanorods (TiO₂NRs), were compared as active components for the fabrication of electro-devices. First both NCs kinds were studied by atomic force microscopy (AFM). The fabricated electro-devices were also investigated by means of AFM in order to analyze the morphology of the nanocomposite layer on the top of the devices. The electrical properties of the fabricated electro-devices were studied by tunneling atomic force microscopy (TUNA) to measure the current at nanoscale passing through the electro-devices and by Keithley semiconductor analyzer to determine the surface conductivity at macroscale. Finally, UV–vis spectroscopy was employed to investigate the UV absorption of the fabricated electro-devices.

2. Experimental

2.1. Materials

The block copolymer used in this work was polystyrene-block-poly(methyl methacrylate) (PSMMA), from Polymer Source, with a polydispersity index (Mw/Mn) of 1.17 and number-average molecular weights of PS and P MMA blocks of 83,000 and 92,500 g/mol, respectively. For the synthesis of both TiO₂ NSs and TiO₂ NRs, titanium tetraisopropoxide (TTIP, 99.999%), trimethylanino-N-diethylene dihydride (TMAO, 98%), oleic acid (OLEA, 90%) and ethyleneglycol (EG, 99.8%) were purchased from Aldrich. Toluene, supplied by Labscan, acetone, supplied by Oppac, and 2-propanol and chlorobenzene, supplied by Panreac, were used as solvent. For the fabrication of electro-devices, indium tin oxide (ITO) coated glass (sheet resistivity 8–12 Ω/sq, Aldrich), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevis™ Al 4083) and Poly(3-ethylithiophene-2,5-diyl) (P3HT, Aldrich) were used.

2.2. Synthesis of TiO₂ nanocrystals

Two different kinds of synthesized TiO₂ NCs were employed for the preparation of TiO₂–PSMMA nanocomposites. The synthesis of TiO₂ NSs was performed according to a reported procedure [18]. In a typical synthesis, a mixture of TMAO and OLEA was degassed. Then TTIP was added under nitrogen flow at 100 °C, followed by the EG injection. The slow hydrolysis of the titanium precursor resulted in OLEA-coated TiO₂ NSs, with an average diameter of 5 nm.

On the other hand, TiO₂ NRs were synthesized also following a previously reported method [17–19]. Briefly, TTIP was added to previously degassed OLEA under nitrogen flow at 100 °C. Subsequently, upon rapid injection of TMAO, a fast hydrolysis process started, leading to the formation of OLEA-coated anatase TiO₂ NRs (average size of 3 nm in diameter and 18 nm in length). The obtained TiO₂ NRs were precipitated from the reaction mixture upon the addition of methanol, isolated by centrifugation and redispersed in toluene.

2.3. Preparation of TiO₂–PSMMA nanocomposites

TiO₂–PSMMA nanocomposites were prepared following a protocol published elsewhere [17]. Firstly, PSMMA block copolymer solutions were prepared by dissolving a defined amount of block copolymer in toluene to reach a concentration of 5 mg/mL. The solution was left under magnetic stirring until a homogeneous mixture was obtained. Then, an adequate volume of TiO₂ NS or TiO₂ NR solution in toluene was added to the block copolymer solutions in order to obtain TiO₂–PSMMA nanocomposites at increasing TiO₂ NC content, namely 50, 60 and 70 wt%. Nanocomposite solutions were stirred for a few hours.

2.4. Fabrication of ITO-glass/PEDOT:PSS/P3HT/TiO₂–PSMMA electro-devices

ITO coated glass substrate was firstly cleaned by sonication in deionized water for 15 min, followed by sonication in acetone for 30 min, sonication in 2-propanol for 30 min and finally sonication in deionized water again for 30 min. Electro-devices were fabricated as follows. Two PEDOT:PSS layers were spin-coated (Spin-coater model P6700 from Specialty Coating Systems, Inc.) onto previously cleaned ITO glass substrate and subsequently dried at 120 °C for 10 min under vacuum. Then, the P3HT layer was deposited by spin-coating a 15 mg/mL P3HT solution in chlorobenzene onto the PEDOT:PSS layer. The films were dried at 140 °C for 15 min. Finally, the TiO₂–PSMMA nanocomposite layer was spin-coated. For comparison, electro-devices based on pristine TiO₂ NSs and TiO₂ NRs, respectively, as last active layer of electro-device, were also fabricated. All layers were deposited at 2000 rpm for 120 s.

2.5. Techniques

The morphology of as-synthesized TiO₂ NSs and TiO₂ NRs onto silicon wafer substrate as well as onto conductive electrodes was studied by atomic force microscopy (AFM) under ambient conditions. AFM images were obtained with a Nanoscope IIIa scanning probe microscope (Multimode, Digital Instruments). Tapping mode (TM) was employed in air using an integrated tip/cantilever (125 μm in length with ca. 300 kHz resonant frequency). Typical scan rates during recording were 0.7 to 1 line/s using a scan head with a maximum range of 15 × 15 μm. Several replicates were prepared per each electro-device and different zones per each sample were investigated by AFM, in order to assess the uniformity of the films. The TiO₂ NS and TiO₂ NR thin films onto silicon wafer were analyzed upon exposure to 254 nm UV light (XX-155, UVP Inc.) for 24 hours in order to remove the organic coating of the NCs. AFM investigation was also carried out on purposely scratched samples to measure the thickness of various systems. Therefore the thickness of the prepared systems resulted in 175±5 nm for those based on pristine TiO₂ NCs, whereas it was 93±5 nm for the TiO₂–PSMMA nanocomposite films. All measured films were deposited onto an ITO layer, which is 120-160 nm thick according to the supplier specifications.

The size and shape of as-synthesized TiO₂ NSs and TiO₂ NRs was analyzed by transmission electron microscopy (TEM). A Tecnai G2 20 Twin transmission electron microscope operated at 200 kV with a resolution of 2.5 Å was used. Both TiO₂ NS and TiO₂ NR were deposited by drop casting onto carbon-coated copper grids.
UV–vis absorption spectra of the fabricated devices were recorded by using a spectrophotometer (Shimadzu UV-3600) in the range between 200 and 800 nm. Quantitative nanoelectrical properties of the investigated electro-devices were measured by using tunneling atomic force microscopy (TUNA) with a Dimension Icon scanning probe microscope equipped with Nanoscope V controller (Bruker). The measurements were carried out using PeakForce TUNA (PF-TUNA) mode under ambient conditions and applying -6 V and 6 V voltages. The PF-TUNA probe was equipped with a Pt/Ir coating tip. Semiconductor characterization system (Keithley model 4200-SCS) was used to study the surface conductive properties of the investigated electro-devices. Two-point experiments were carried out applying a voltage sweep from -6 to 6 V to study the conductive properties at the macroscopic level. The sheet resistivity was measured by a four-point collinear probe method with 100 mA current.

3. Results and discussion

Both TiO2NSs and TiO2NRs were synthesized by means of a colloidal chemistry procedure [18,19], which allowed to obtain organic surfactant coated NCs with controlled size and shape. In order to determine the size and shape of used nanocrystals, both AFM and TEM were employed. For AFM, the thin films were prepared by spin-coating each NC type solution onto prewashed silicon wafer substrates and exposing them to UV light for 24 hours. This treatment allows to remove the organic capping layer of the NCs and to analyze the size and shape of inorganic NCs. Fig. 1 shows the AFM phase images of TiO2NSs and TiO2NRs and the corresponding TEM micrographs. In both AFM and TEM images, TiO2NCs are clearly observed, and the spherical and rod-like shape can be distinguished in each image, respectively. NC size was determined as around 5 nm diameter for TiO2NSs and around 3 nm diameter and 18 nm length for TiO2NRs, in agreement with previous reported values [19,20]. The micrographs showed both TiO2NSs and TiO2NRs homogeneously dispersed on the whole surface.

In the fabricated electro-device [3,4], TiO2 acts as the carrier transport material, whereas P3HT is an effective hole transport material in its regioregular form [5]. The combination of polymers with inorganic semiconductors like TiO2NCs favors the charge transfer between the high electron affinity inorganic semiconductor and the relatively low ionization potential organic molecules and polymers [21–23]. The top layer of the devices was the one that was varied in order to investigate the effect of each kind of TiO2 NCs and their content on the electrical properties of the electro-devices.

Prior to the study of the electro-devices based on TiO2–PSMMA nanocomposites, systems based on pristine TiO2NS and TiO2NR films, respectively, as top layer, were preliminarily investigated as references. The morphology was studied by AFM and the electrical properties at nanoscale were performed by AFM in the PeakForce TUNA mode, as shown in Fig. 2. The AFM phase images for the electro-devices based on TiO2NSs and TiO2NRs, respectively, pointed out a very similar morphology in the two cases, with white spots, ascribable to TiO2NCs, well dispersed on the surface. TUNA measurements performed on the same samples highlighted that no response could be detected in any electro-device (results not shown here) when a negative voltage (−6 V) was applied to the TUNA tip. On the contrary, applying a positive voltage (+6 V) to the tip, both the TiO2NS and TiO2NR based systems exhibited TUNA currents passing through the sample, presenting the devices with TiO2NRs higher local current values. The presence of TUNA currents was clearly related to the presence of TiO2NCs since the conductive spots are noticeably in accordance with the bright spots in both AFM phase images of electro-devices based on TiO2NS and TiO2NR active layer. Thus, conductive spots appeared uniformly dispersed on the surface of both devices. The current profiles corresponding to a horizontal cross section of the TUNA images, and accounting for currents of the order of pA, are reported in Fig. 2. They show that the current passing through the TiO2NR based device is higher than that recorded for the TiO2NS based sample. Such evidence allows to infer a different behavior of the two differently shaped NCs, that can be attributed to the different geometry of the NRs that enables more effective percolation paths for electrical transport, in agreement with the report by Huynh et al. [5].

The electro-devices based on TiO2–PSMMA nanocomposites were studied by AFM and TUNA. AFM phase images of ITO-glass/PEDOT:PSS/P3HT/TiO2NS–PSMMA and ITO-glass/PEDOT:PSS/P3HT/TiO2NR–PSMMA electro-devices prepared at increasing TiO2 contents (50, 60 and 70 wt%) are presented in Fig. 3. The images showed regular and homogeneous surfaces where TiO2NSs and TiO2NRs appeared well-dispersed visible as small white spots. The surfaces presented distinctive nanostructured morphology. The surface morphology of the investigated systems, namely based on TiO2NS–PSMMA and on TiO2NR–PSMMA nanocomposites, respectively, results significantly different, although the surfaces of both systems presented a distinctive nanostructured.

![Fig. 1. AFM phase images (3 μm x 3 μm with inset of 0.5 μm x 0.5 μm on the right) of TiO2NSs (a) and TiO2NRs (b) onto silicon wafer substrates. The insets on the left correspond to the TEM micrographs of TiO2NSs (a) and TiO2NRs (b).](image-url)
Fig. 2. AFM phase images (3 μm x 3 μm with inset of 0.5 μm x 0.5 μm) and TUNA images (3 μm x 3 μm) taken at 6 V of ITO-glass/PEDOT:PSS/P3HT/TiO2NS (a, b) and ITO-glass/PEDOT:PSS/P3HT/TiO2NR (c, d) electro-devices, respectively. The graphs correspond to the current profile marked on the TUNA images.

Fig. 3. AFM phase images (3 μm x 3 μm) of ITO-glass/PEDOT:PSS/P3HT/TiO2NS-PSMMA electro-devices fabricated with 50 (a), 60 (b) and 70 (c) wt% TiO2NS-PSMMA nanocomposites and ITO-glass/PEDOT:PSS/P3HT/TiO2NR-PSMMA electro-devices fabricated with 50 (d), 60 (e) and 70 (f) wt% TiO2NR-PSMMA nanocomposites.
morphology. Indeed, some brighter spots present on the surface and ascribable to NCs present a different shape and size in the two distinct sets of samples. In particular for the TiO$_2$NS based devices some brighter islands were randomly distributed on the surface, conversely the morphology of the TiO$_2$NR based systems appeared more regular and the surface is homogeneously covered by the NRs. Clearly, while the overall morphology of the systems accounts for all the layers forming the system, the top layer nanocomposite morphology particularly affects the electro-device characteristics.

TUNA images and current profiles of the ITO-glass/PEDOT:PSS/P3HT/TiO$_2$NS-PSMMA electro-devices with different contents of TiO$_2$NS content, applying 6 V, are reported in Fig. 4. In this case, similarly to what is observed for the pristine TiO$_2$NC systems, negative voltage did not result in any current response (results not shown here). On the contrary, when a positive 6 V voltage was applied, some small local currents, with values lower than 1 pA were detected through the samples. These local currents are found to correspond to the dark spots appearing in the TUNA images, being related again to the presence of the TiO$_2$NSs.

TUNA images and current profiles of the ITO-glass/PEDOT:PSS/P3HT/TiO$_2$NR-PSMMA electro-devices obtained applying 6 V are shown in Fig. 5. For devices fabricated using TiO$_2$NR-PSMMA nanocomposites, also in this case, no response was detected for a negative voltage applied to the TUNA tip, whereas switching to a positive voltage, a significant response was detected. TUNA images clearly showed bright conductive areas almost all over the surface of the electro-devices based on the nanocomposites containing 50, 60 and 70 wt% TiO$_2$NRs, respectively. These bright areas appeared as islands on the investigated surfaces, and their position is in agreement with the morphology detected in the AFM images, as the areas with the highest TUNA currents correspond to those where aggregated of TiO$_2$NRs are present, while dark areas do not provide any response to the applied voltage.

![Fig. 4. TUNA images (3 μm x 3 μm) taken at 6 V of ITO-glass/PEDOT:PSS/P3HT/TiO$_2$NS-PSMMA electro-devices fabricated with 50 (a), 60 (b) and 70 (c) wt% TiO$_2$NS-PSMMA nanocomposites. The graphs correspond to the current profile marked on the TUNA images.](image-url)
The current values reported in the TUNA current profiles showed current values remarkable higher for devices based on TiO$_2$NRs than for the TiO$_2$NSs based counterparts, confirming the beneficial effect of the rod-like shape in forming effective percolating pathways, and thus improving charge transport in electro-devices such as in particular photovoltaic devices [5,18,20]. However, the TUNA measurements did not show a dependence on TiO$_2$NR content in the top layer of each electro-device. In fact, the 50 wt% TiO$_2$NR-PSMMA based device showed the highest current value, while the lowest value was recorded for the 70 wt%
TiO$_2$NR-PSMMA based one. This feature could be accounted for by the fact that a very high NC content can turn in a more extended formation of large aggregates, and, consequently in less efficient conductive paths.

Scheme 1 describes the conductive behavior of fabricated electro-devices, with TiO$_2$NS and TiO$_2$NR based nanocomposites. The different geometry of NSs and NRs impacts in the final morphology of the electro-devices fabricated from the two types of nanocomposites, based on one or the other kind of NC. Indeed, the electro-devices fabricated with TiO$_2$NRs are definitely more prone to assembly in the host polymer to form effective pathway, as demonstrated by the current values detected for this type of device (20-300 pA approximately). The comparison of the experiments performed on the reference samples, based on pristine TiO$_2$NRs, suggests that the incorporation of the NRs into the host block copolymer results in effectively directing the NRs organization in a highly interconnected structure, which turns much more effective in electrical transport and hence ultimately in a device with higher currents [23,24].

Conductive properties at macro-scale of fabricated electro-devices were measured by means of a Keithley semiconductor analyzer operating in two-point mode. Current-voltage (I-V) curves for each sample were recorded by applying a voltage sweep between -6 and 6 V. Fig. 6 shows the current-voltage curves corresponding to all investigated electro-devices. Devices fabricated using TiO$_2$NS based nanocomposites (Fig. 6a) as top layer presented curves with very low current intensity for voltages between -6 and 6 V, being up to 600 pA. Conversely, devices based on TiO$_2$NR-PSMMA nanocomposites (Fig. 6b) displayed higher intensity currents, up to 30 nA, thus further confirming the efficiency of TiO$_2$NRs as charge carriers higher than that of TiO$_2$NSs, due to their specific geometry [5,18]. The comparison with the reference systems based on pristine TiO$_2$NS and TiO$_2$NR film, respectively, as a top layer, points out very low currents, although those based on TiO$_2$NRs show slightly higher currents, anyway not higher than 200 pA. Therefore, these evidences strongly highlight the role of the PSMMA block copolymer in directing the organization of the NCs into superstructures able to enhance the inter-particle connection, and thus generate effective percolating networks for charge carrier transport, ultimately affecting the conductivity of the systems [23,24]. Interestingly the trends of the results obtained by TUNA measurements and by using the semiconductor analyzer are in agreement, in spite of the fact that the two techniques accounts, in fact, for different phenomena, namely the current on the investigated film surfaces, hence a macroscale measurement, and the current through the whole electro-devices, that is detected at nanoscale.

The electro-devices based on TiO$_2$NRs containing nanocomposites, that presented the highest intensity current, were then also analyzed by the four-point collinear probe method with the Keithley semiconductor analyzer in order to determine the sheet resistivity of the devices [25,26]. Sheet resistivity allows to easily calculate the electrical resistivity as well as the electrical conductivity of the investigated devices (Table 1). The lowest sheet resistivity and the highest conductivity values were found for the 60 wt% TiO$_2$NR-PSMMA nanocomposite based electro-device, whereas the highest sheet resistivity and the lowest conductivity was for the 50 wt% TiO$_2$NR-PSMMA nanocomposite device. In general the values obtained for sheet resistivity are of the same order of magnitude of the values reported in literature for composite films containing TiO$_2$ nanoparticles [27].

The absorption spectra of all fabricated electro-devices are shown in Fig. 7. All UV–vis spectra exhibited an absorption in the region below 650 nm, which can be ascribed to the $\pi-\pi^*$ transition of the P3HT, and an intense feature can be detected in the UV region below 400 nm, attributed to the TiO$_2$NCs. The influence of the type and content of TiO$_2$NCs can be noticed in the absorbance intensity in the range 400-650 nm, that can be found proportional to the TiO$_2$ content, both in the case of TiO$_2$NSs and TiO$_2$NRs, being the difference between the two not very high. Since both kinds of NCs showed a similar absorbance spectrum [18], and the P3HT concentration was always kept the same for the preparation of all devices, the difference here could be explained considering all layers of the analyzed devices and the interaction effect among them. Moreover, there is another appreciable difference comparing both kinds of nanoparticles, in the case of the most intense absorption. TiO$_2$NR based electro-devices showed the intense absorption at slightly higher wave-lengths (400 nm) than TiO$_2$NS (360 nm). In any case, these differences were not very significant and it can be claimed that these electro-devices have an absorption range from visible to ultraviolet, which agrees well with solar irradiation [28]. It is worthwhile to point out that the presence of nanocrystalline TiO$_2$ strengthens the UV absorption of P3HT, thus making the nanocomposites more suited for solar energy conversion based application.
Table 1
Sheet resistivity, thickness, electrical resistivity and conductivity values calculated for the selected electro-devices.

<table>
<thead>
<tr>
<th>Electro-device</th>
<th>Sheet resistivity (Ω/sq)</th>
<th>Thickness (cm)</th>
<th>Electrical resistivity (Ω·cm)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO-glass/PEDOT:PSS/P3HT/50 wt% TiO2 NS-PSMMA</td>
<td>43.33 ± 10.19</td>
<td>2.33 × 10^{-5}</td>
<td>1.01 × 10^{-4}</td>
<td>990.57</td>
</tr>
<tr>
<td>ITO-glass/PEDOT:PSS/P3HT/60 wt% TiO2 NS-PSMMA</td>
<td>37.34 ± 4.77</td>
<td>2.33 × 10^{-5}</td>
<td>8.70 × 10^{-4}</td>
<td>1149.53</td>
</tr>
<tr>
<td>ITO-glass/PEDOT:PSS/P3HT/70 wt% TiO2 NS-PSMMA</td>
<td>38.94 ± 6.28</td>
<td>2.33 × 10^{-5}</td>
<td>9.07 × 10^{-4}</td>
<td>1102.20</td>
</tr>
</tbody>
</table>

* Values directly calculated from the four-point probe measurements.
* \( p = \text{Rs} - t \) (\( p \): electrical resistivity, \( Rs \): sheet resistivity, \( t \): thickness).
* \( \sigma = 1/(p t) \) (\( \sigma \): conductivity).

4. Conclusions

Different electro-devices were successfully fabricated using TiO2 NCs embedded in the PSMMA host matrix in order to investigate the influence of the TiO2 NC geometry and content on the electrical properties of the resulting systems. For this purpose, organic capped TiO2 NCs were prepared in spherical and rod-like shape, respectively, and embedded in PSMMA copolymer at increasing contents and using such nanocomposites as top layers in electro-devices. In addition, reference systems were prepared by using pristine TiO2 NCs.

The AFM surface characterization of the top layer of all prepared electro-devices showed NCs dispersed on the whole investigated surface, and, in particular, the nanocomposites based systems displayed nanostructured morphology, accounting for the templating role of PSMMA host in directing the organization of TiO2 NCs, regardless of their shape.

UV-vis absorption spectra assessed the optical characteristics of the prepared electro-devices, showing that the TiO2 strengthens the absorption in the UV range, thus widening the range of solar spectrum available for energy conversion applications. The electrical properties of electro-devices were investigated at nanoscale by TUNA and at macroscale by Keithley semiconductor analyzer. Results indicated that electro-devices fabricated using TiO2 NRs presented higher current and conductivity values than those obtained using TiO2 NSs. Moreover, the presence of block copolymer improved the electrical response in comparison to samples prepared with the pristine NCs.

The electrical and optical properties of the TiO2/NR-PSMMA nanocomposites based electro-devices proved that the use of block copolymer leads to a morphological control on the inorganic semiconductor NC organization, resulting in a more effective percolation path, particularly beneficial for enhancing carrier transport and thus conductivity, features that can be conveniently exploited in a variety of energy conversion applications, including innovative solar cell fabrication.

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