Influence of TiO₂ nanoparticles on the optical and structural properties of PPV thin films converted at low temperatures

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Abstract. In this work we studied the optical properties of poly(p-phenylene vinylene) (PPV) produced by the thermal conversion of a precursor polymer blended with a synthetic dye (Reactive Black 5). The production of PPV by this method decreases the overall time and cost of the process. We observed that the introduction of the dye resulted in an additional absorbance band near 550–700 nm, which can be beneficial to the photon harvesting capacity of the polymer if it is used as the donor material in a photovoltaic device. We studied how the optical and structures properties of this blend change when different quantities of TiO₂ nanoparticles are introduced. For that, thin films were produced by the cast deposition of pre-PPV:dye:TiO₂. The scanning electronic microscopic images showed that the inorganic semiconductor form large agglomerates of approximately 200 nm, indicating a very rough surface where the dye can be adsorbed. The analysis of photoluminescence and Raman peaks indicated a reduction of the mean conjugation length of the polymer chains in the presence of TiO₂ nanoparticles.

Keywords: polymer composites, nanomaterials, PPV and dye

1. Introduction

Organic electronics is one of top rising research fields nowadays, the understanding of how we can manipulate organic materials and their physical properties have opened field to several applications, e.g. organic solar cells [1, 2], OLEDs [3, 4], etc. Some of these devices, like the dye-sensitized solar cell [5], put together organic compounds and inorganic semiconductor nanoparticles in order to absorb sunlight and transport charge carriers. The inclusion of metallic or semiconductor nanoparticles changes the optical properties of the polymers [6–11], resulting in new characteristics of the materials that can be explored to technologic applications. In this sense, knowing how inorganic nanoparticles influence organic materials is extremely important. Even with its relatively low conductivity, poly(p-phenylene vinylene) (PPV) is one of the conjugated

polymers used in solar cell fabrication [12, 13]. Its precursor, poly(p-xylylene tetrahydrothiophenium chloride) (PTHT), is soluble in water, a characteristic that is getting increasing importance due to the increasing concern on environmental and safety problems related to the organic solvents [12, 14–16]. The thermal treatment of PPV's precursor is the conventional route to produce PPV, but the resulting film has some chain defects, due to the high temperatures (above 200°C) used, undermining its conductivity [17]. In addition, high temperature severely affects the properties of indium-tin oxide (ITO)/polymeric layer interface, as reported by Poças *et al.* [18]. To reduce the harmful effect of the thermal treatment, PPV can be produced by an alternative route in which a compound having a SO₃[−] group is incorporated [19] (Figure 1). These compounds replaces the chloride anions present on

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Figure 1. Conventional and alternative route of PPV's production (a). Chemical structure of Reactive Black 5 (b).

the precursor with the radical SO_3^- , facilitating the thermal elimination and reducing the thermal energy activation [19]. Many synthetic dyes exhibit this group and have been used to help the conversion of PPV [20].

In this work we used the dye Reactive Black 5 to produce PPV thin films from the alternative route proposed by Marletta *et al.* [19, 20]. It was observed that, in addition to allowing the conversion of the PPV precursor at lower temperatures, the PPV:dye film presented an absorption band extended to longer wavelengths, which is broader than absorbance of PPV produced without the dye. This can be beneficial to light harvesting capacity of this compound, if it is used as donor material in an active layer of a photovoltaic device. Different amounts of TiO_2 (acceptor material) were then added to the polymer solution, to see how this mixture reacts in the presence of inorganic nanoparticles. All components, dissolved in aqueous solution, were cast-deposited to form a bulk layer film, and the optical and structural properties of these blends were investigated by absorbance, photoluminescence (PL), Raman scattering and Scanning Electron Microscopy (SEM) techniques.

2. Experimental procedures

All solutions and films were prepared under ambient conditions, using ultrapure water (resistivity 18.2 $\text{M}\Omega/\text{cm}$). Reactive Black 5 (code 306452) and PTHT (code 540765) were purchased from Sigma-Aldrich (USA) and TiO_2 nanoparticles (P25 Aerox-

ide; 70/30 anatase/rutile; $d \approx 20$ nm) from Evonik-Degussa (Germany). The mixing ratio between PTHT and dye was 1:1 (mol/mol), and their molarities were $1.25 \cdot 10^{-3}$ M. The concentration of TiO_2 solution was 2 mg/mL. All solutions were first magnetically stirred for 15 min and put at ultrasonic bath for another 15 min. After mixing PPV's precursor, Reactive Black 5 and TiO_2 , the resulting solution was again magnetically stirred and put at ultrasonic bath. The following samples were made using glass as substrate: (a) 100 μL PTHT/dye; (b) 100 μL PTHT/dye + 10 μL TiO_2 ; (c) 100 μL PTHT/dye + 50 μL TiO_2 ; (d) 100 μL PTHT/dye + 200 μL TiO_2 . All samples were cast-deposited and stored, protected from any light, for the period of 24 hours for water evaporation. After that, the samples were heated at 110°C for 30 minutes in air and in a home-made oven, according to [20]. The UV-Vis absorbance was measured by using a DT-Mini-2-GS model UV-Vis lamp and an USB-4000 minispectrometer (Ocean Optics). The same spectrometer was used to detect the PL of the films, whereas a solid-state laser ($\lambda = 405$ nm) was used as excitation source. During the PL measurements, the samples were under rough vacuum (10^{-2} mbar). The Raman spectra were obtained with a portable spectrometer Raman Advantage532[®] from Delta Nu, excited in 532 nm. NuSpec software from Delta Nu was used, making use of baseline resources, in order to remove the background fluorescence. To make SEM images, first an Au layer of approximately 40 nm was deposited using Bal-Tec SCD OSO sputter coater.

SEM images were made using FEI Quanta 200 SEM. All measures were performed at room temperature.

3. Results and discussion

The normalized absorbance of pure PPV, samples (a) and (b), all made by the alternative route are shown in Figure 2. This route reduces the preparation time and overall cost of the sample, since it uses a faster thermal treatment at lower temperature when compared to the conventional route. The maximum of the absorption, near 450 nm, is a signature of converted PPV. The absorption band in 550–700 nm is only present when the dye is introduced, since standard PPV ends its absorption near 530 nm [21]. This extra absorption band can increase the quantity of photons collected in the farther region of the solar spectrum, offering the possibility to enhance the overall efficiency of photovoltaic devices. The introduction of TiO₂ nanoparticles increases the thin films opacity, as seen in Figure 2 (black curve, baseline corrected). However, the PPV absorption band (~450 nm) and the dye absorption band (~650 nm) are still present. After the thermal treatment of 110°C, PPV+dye films exhibit characteristics of PPV made by the conventional route [21].

The Raman spectra of all samples made in this work are shown in Figure 3. Also the spectra of pure PPV film and of the dye aqueous solution were included in this figure. The pure PPV sample was made with

Figure 2. Normalized absorbance of pure PPV (line with circles), samples with 0 (a) and 10 μL (b) of TiO₂ (red and black lines, respectively). All samples were produced following the alternative route. The pure PPV sample was made using DBS (sodium dodecylbenzenesulfonate) as SO₃⁻ compound. The baselines of all spectra were corrected.

Figure 3. Raman spectra of the samples. Anatase and rutile peaks of TiO₂ are only visible in the range of 600 cm^{-1} (not showed here).

the 1:1 mol/mol proportion between PTHT and DBS (sodium dodecylbenzenesulfonate) [19].

The assignments of the most important Raman peaks are shown in Table 1 [22–24]. The peaks at 1284 and 1496 cm^{-1} are exclusive from the dye, since the naphthalene group and the C–N bond are only present in Reactive Black 5's structure. The introduction of TiO₂ nanoparticles leads to an increase of intensity of these peaks, suggesting that a portion of dye molecules is remaining intact after the thermal treatment. Another important aspect is the behavior of the peak at 1170 cm^{-1} , which is exclusive from PPV. Its intensity decreases as the quantity of TiO₂ increase, showing that less converted films are produced. This indicates that a portion of dye molecules can be adsorbed on the surface of TiO₂ and is not participating in the chemical reaction with the PPV precursor.

We believe that the dye is adsorbing in the TiO₂'s very rough surface, since its particles dimensions are in the range of 20 nm. These small particles however, form large clusters of approximately 200 nm, as shown in SEM image of sample (d) (Fig-

Table 1. Assignment of important peaks of Raman spectra of samples [22–24]

Wavenumber [cm^{-1}]	Attribution
1170	C–C stretching + C–H bending of the phenyl ring
1284	C=C stretching of the naphthalene group
1323	C=C stretching + C–H bending of the vinyl group
1496	C–N vibration
1550	C=C stretching of the phenyl ring
1585	C–C stretching of the phenyl ring
1625	C=C stretching of the vinyl group

Figure 4. SEM images of TiO_2 nanoparticles in sample d). The large clusters (around 200 nm) are formed by the small particles (approximately 20 nm).

ure 4). We observed, as expected, that as the amount of TiO_2 increased, the number of clusters also increased. Although these large clusters can result in films with high surface roughness, the polymer could easily penetrate this matrix and have a substantial contact with the inorganic particles, which is extremely important to rapidly dissociate the excitons [25].

The presence of TiO_2 interferes in the photoluminescence spectra, as seen in Figure 5. Even the smallest quantity results in a blue-shift of approximately 17 nm. As the number of nanoparticles increases, the photoluminescence intensity increases up to 7 times. This is contrary to the PL quenching expected due to donor-acceptor interaction [7, 12, 14, 26, 27]. However, the PL enhancement was also

observed in other works using different materials mixed with PPV [28–30].

Son *et al.* [31] and Zhang *et al.* [32] showed that a break on the conjugation length of PPV leads to an enhanced photoluminescence. In the work of Son, they engineered cis linkages into the PPV chain. These cis linkages interrupt the conjugation and interfere with the packing of the polymer chains, resulting in a gain of photoluminescence [31]. Zhang *et al.* made several thermal treatments on PPV's precursor using different temperatures. They observed that as the temperature increases, the PL intensity decreases, indicating that partially conjugated PPV have enhanced photoluminescence [32]. Our observations corroborates with these works: both PL blue shift and enhanced PL intensity is showing that PPV:dye mixed with TiO_2 results in smaller conjugated segments than pure PPV. The presence of dye molecules adsorbed on the TiO_2 surface, as suggested by the results of Raman scattering, may indicate that the amount of dye participating in the ion exchange with the pre-PPV decreased, resulting in less conjugated PPV chains after the thermal conversion, which explains the PL blue shift. Moreover, the formation of large agglomerates of TiO_2 may be affecting the inter-chain polymer interaction, resulting in a greater localization of the photo-generated carriers and therefore increasing the PL intensity. Thus, both agglomeration of TiO_2 nanoparticles and the availability of dye molecules to participate in the PPV conversion process must be controlled to produce PPV:dye: TiO_2 blends in which the polymer chains have larger effective conjugation length.

Figure 5. Photoluminescence spectra (a) and normalized photoluminescence spectra (b) of the samples

4. Conclusions

PPV thin films were produced by an alternative route, adding Reactive Black 5 dye to the precursor polymer solution. The dye enabled the conversion of PPV at lower temperatures than that used conventionally, and led to a gain of absorption at the region of 550–700 nm, where the pure PPV is optically inert. Raman scattering analysis showed that more dye molecules remain intact after the thermal conversion when TiO₂ nanoparticles are incorporated into pre-PPV:dye mixture. The SEM images showed the formation of TiO₂ agglomerates with diameter around 200 nm. The enhanced intensity and the blue-shift observed in the PL spectra were due to the formation of partially conjugated PPV when TiO₂ is introduced. However, the additional absorption band towards longer wavelengths increases the light harvesting capacity of the film, therefore enhancing the possibility to use this blend as active layer in free organic solvent photovoltaic devices.

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