

## Optical and electrical properties of PPV/SiO<sub>2</sub> and PPV/TiO<sub>2</sub> composite materials

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### Abstract

Composites made by incorporation of SiO<sub>2</sub> or TiO<sub>2</sub> nanoparticles into poly(*p*-phenylene vinylene) (PPV) have been fabricated and their optical and electrical properties have been investigated. The UV–vis absorption band of the composite films showed a large blue-shift with SiO<sub>2</sub> nanoparticles, but only little difference with TiO<sub>2</sub> nanoparticles. Photoluminescence (PL) spectra showed the same blue-shift trend for SiO<sub>2</sub> composites, and in addition, an increase in intensity of the high energy shoulder (515 nm) when the concentration of nanoparticles increased. Raman spectra showed a reduction of the 1547/1625 cm<sup>-1</sup> band ratio in SiO<sub>2</sub> composites but not in TiO<sub>2</sub> ones. These results suggest that SiO<sub>2</sub> nanoparticles reduced the PPV conjugation length, while TiO<sub>2</sub> nanoparticles did not. For SiO<sub>2</sub> particles, the reduction of conjugation lengths is more pronounced on increasing the oxide concentration or on decreasing the particle size. Fourier-transform Infrared (FT-IR) spectra showed that both types of nanoparticles reduced the formation of carbonyl groups in PPV main chains. Current-voltage characteristics measured in ITO–composite–MgAg diodes exhibit different electrical behavior of the composites depending on the particle size and the nature of the oxide. The composite-electrode contact morphology, the polymer–dielectric particle contact and the change in the polymer chain length are the possible explanations for these changes in behavior of the diodes.

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### 1. Introduction

Conjugated polymers are nowadays used in several display applications [1–4], resulted from intensive research works over the last decade since the first report on polymer-based light emitting diodes [5]. Among them, poly(*p*-phenylene vinylene) (PPV) and its derivatives have attracted a great deal of attention because of their particular structure and their highly interesting electroluminescent properties [6]. To enhance the performance of PPV-based devices, several studies have been carried out on composites made with polymers and nano-oxide particles such as silicon oxide (SiO<sub>2</sub>) or titanium oxide (TiO<sub>2</sub>). The former is found to have a good effect on the conductivity of the polymer host while the second can influence its photovoltaic properties. The use of composites is believed to increase the electrical conduction of the polymer [7] and in addition, to

improve its stability [8], which is of prime importance in devices. For both oxides, modifications of the polymer luminescence were observed. However, contradictory results have been reported. For example, poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) blended with SiO<sub>2</sub> was found to have an improved conductivity as compared to the bare polymer [9], while PPV with similar nanoparticles shows a lower conductivity than the polymer alone [10].

Besides, the effects of the nanoparticles on the structure of the polymer are still a subject of research. Baraton et al. [11] found that blends using TiO<sub>2</sub> nanoparticles do not break the PPV conjugation and possess the potential of gas sensing applications. Zhang et al. [12] observed that the TiO<sub>2</sub> nano-aggregates took the form of a sphere and finally ellipsoid with an alignment, as the content of TiO<sub>2</sub> increased.

In this work, we have studied some composites made by incorporation of SiO<sub>2</sub> or TiO<sub>2</sub> nanoparticles of different concentrations and sizes in PPV. We have examined the optical and electrical properties of the hybrid materials

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using the same polymer host in order to check the influence of the nature and the size of the particles on the behavior of the composites.

## 2. Experimental

The precursor polymer of PPV was prepared by the classical Wessling–Zimmermann method reported previously [13]. SiO<sub>2</sub> nanoparticles dispersed in ethylene glycol (EG) were provided from SPCI S.A. and TiO<sub>2</sub> nanoparticles from Degussa. Dispersion of nanosized TiO<sub>2</sub> was carried out in distilled water under ultrasonication for 8 h. All SiO<sub>2</sub> and TiO<sub>2</sub> dispersed solutions were filtered with a 10- $\mu$ m filter.

Four PPV precursor solutions were mixed with diameter 100 nm SiO<sub>2</sub>/EG solutions in different weight ratios (1, 2, 4 and 8%). The mixtures were prepared under ultrasonication for 1 h and then spin-coated on the pre-cleaned glass substrates. The thermal conversion of the precursor films was performed under vacuum at 300 °C for 3 h. Four other PPV/SiO<sub>2</sub> nanocomposites (20 nm, 1, 2, 4 and 8%) and four PPV/TiO<sub>2</sub> nanocomposites (20 nm, 1, 2, 4 and 8%) were prepared by the similar procedure.

UV–vis absorption spectra of the samples were measured with a CARY 5G spectrophotometer. FT-IR and Raman experiments were performed by using a BRUKER IFS 28 and a BRUKER RFS 100 spectrophotometer, respectively. Photoluminescence (PL) spectra were obtained with a Fluorolog 3 spectrophotometer.

Diodes were prepared by depositing the composite thin film onto indium tin oxide (ITO) substrates followed by thermal evaporation of MgAg cathode of thickness 500 nm. Current–voltage (*I*–*V*) characteristics of devices were recorded using a setup already described [14] and were performed with the samples in vacuum and at room temperature.

## 3. Results and discussion

### 3.1. UV–vis spectra

For pristine PPV, the maximum of the absorption band was found at 433 nm. In PPV/SiO<sub>2</sub> composites of different oxide concentrations, the UV–vis absorption peaks were from 430 to 419 nm with 100 nm SiO<sub>2</sub> particles, and from 426 to 403 nm with 20 nm SiO<sub>2</sub> particles. The shift in energy became larger as the content of SiO<sub>2</sub> increased. This variation suggests that SiO<sub>2</sub> nanoparticles would reduce the conjugation lengths of PPV, and the reduction becomes significantly important as the content of SiO<sub>2</sub> increases. Besides, we observe that smaller nanoparticles induce a larger blue-shift for an identical oxide concentration. It is possible that smaller nanoparticles are inserted in polymer chains more easily and produce a greater hindrance thus reduce the conjugation lengths.

Similarly, in PPV/TiO<sub>2</sub> composites of different oxide concentrations, the UV–vis absorption peaks were from 429 to 426 nm. As the shift is small, TiO<sub>2</sub> nanoparticles apparently have little or no effect on the conjugation of PPV. This result is in agreement with that obtained by Zhang et al. [12] who found that the absorption of PPV in the nanocomposites was not perturbed by the presence of the TiO<sub>2</sub> nanoparticles.

### 3.2. FT-IR spectra

Fig. 1 shows the FT-IR spectra of PPV and some nanocomposites. In PPV/SiO<sub>2</sub> systems, the band centered at 3450 cm<sup>-1</sup> corresponds to O–H stretching of Si–OH; those at 1107 and 794 cm<sup>-1</sup> were assigned to Si–O–Si asymmetric and symmetric vibrations, respectively [15]. In PPV/TiO<sub>2</sub> composites, one broad band was found at 3445 cm<sup>-1</sup>, which was attributed to O–H stretching of Ti–OH. We also noted a small band at 1107 cm<sup>-1</sup>, which may be related to Ti–O–C stretching mode. Zhang et al. [12] claimed that they observed two additional bands at 1623 and 1105 cm<sup>-1</sup>, which were assigned to Ti–O and Ti–O–C stretching modes. They concluded that Ti organic compound was formed and could result in an alignment structure of TiO<sub>2</sub> particles. In our samples, this alignment was not observed. Scanning electron microscopy images (not shown) support this observation and show a fair homogeneous repartition of the oxide particles in the polymer host matrix.

On the other hand, we notice that the band at 1693 cm<sup>-1</sup> decreases in intensity as compared with that of pristine PPV films. This band is related to the carbonyl groups C=O which were formed during the thermal conversion of the polymer precursor [11]. The decrease in intensity of this band indicates that the presence of TiO<sub>2</sub> nanoparticles

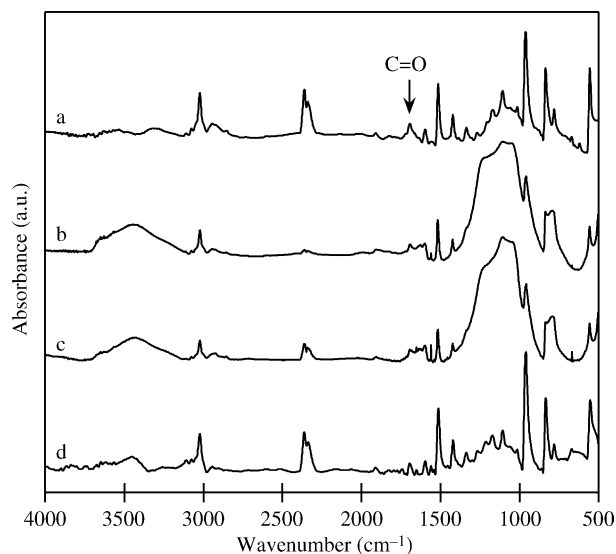


Fig. 1. FT-IR spectra of PPV and nanocomposite thin films: (a) PPV; (b) PPV/SiO<sub>2</sub> (100 nm, 2%); (c) PPV/SiO<sub>2</sub> (20 nm, 2%); (d) PPV/TiO<sub>2</sub> (20 nm, 2%).

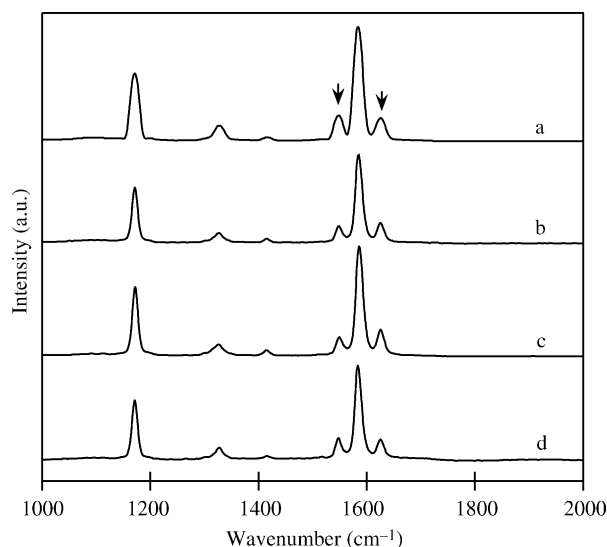


Fig. 2. Raman spectra of PPV and nanocomposite thin films: (a) PPV; (b) PPV/SiO<sub>2</sub> (100 nm, 2%); (c) PPV/SiO<sub>2</sub> (20 nm, 2%); (d) PPV/TiO<sub>2</sub> (20 nm, 2%).

would prevent the oxidation of the PPV chains and the composites would be more stable than the pristine polymer. The IR spectra of PPV/SiO<sub>2</sub> samples showed similar features but the 1693 cm<sup>-1</sup> intensity reduction is smaller.

### 3.3. Raman spectra

Fig. 2 shows the Raman spectra of PPV and some nanocomposites. The main difference between PPV films and its composites is the modification of the triplet between 1500 and 1700 cm<sup>-1</sup>. In PPV films, the intensity of the band at 1547 cm<sup>-1</sup> (band 1) is comparable to that at 1625 cm<sup>-1</sup> (band 3), and the (band 3/band 1) intensity ratio is approximately unity [16]. In all the PPV/SiO<sub>2</sub> composites (100 and 20 nm), this ratio is significantly reduced when the oxide concentration increased. From our previous study on PPV oligomers [16], the change in this triplet is related to the conjugation length of PPV: when the conjugation length is reduced, the intensity of band 3 grows stronger than that of band 1. Hence, the change observed in the composite films suggests that introduction of SiO<sub>2</sub> nanoparticles into PPV would reduce the conjugation length of the polymer chains.

In contrast, the Raman spectra of PPV/TiO<sub>2</sub> nanocomposites are similar to that of pristine PPV films whatever the concentration used. This result suggests that the presence of TiO<sub>2</sub> nanoparticles in the composite film has no effect on the conjugation length of PPV chains.

### 3.4. PL spectra

Figs. 3–5 show the photoluminescence spectra of PPV and the nanocomposites. The main emission band of PPV is located at 551 nm, with two shoulders at 514

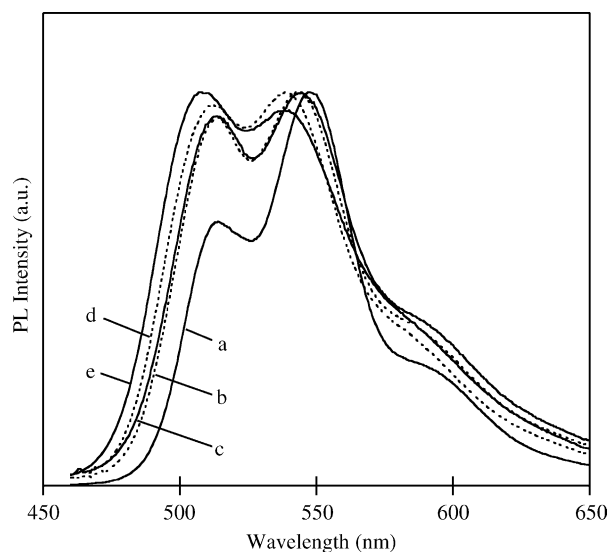


Fig. 3. Photoluminescence spectra of PPV/(100 nm SiO<sub>2</sub>) composite thin films with different particle concentrations: (a) 0; (b) 1; (c) 2; (d) 4; (e) 8%.

and 596 nm. For the PPV/SiO<sub>2</sub> nanocomposites, the main band is blue-shifted from 544 to 538 nm with 100 nm SiO<sub>2</sub> particles, and from 533 to 527 nm with 20 nm SiO<sub>2</sub> particles. The peak shift in energy became larger with increasing concentrations or decreasing particle size. This evolution is compatible with that observed in the UV–vis absorption spectra. We also note an increase in intensity of the 515 nm shoulder, which becomes the dominant emission band as the SiO<sub>2</sub> concentration increases. The enhancement of this band was previously observed in several PPV/nanoparticle composites [17,18]. Two possible explanations were proposed to account for this observation. First, the high energy of the 515 nm peak may indicate that the short segments of the polymers are

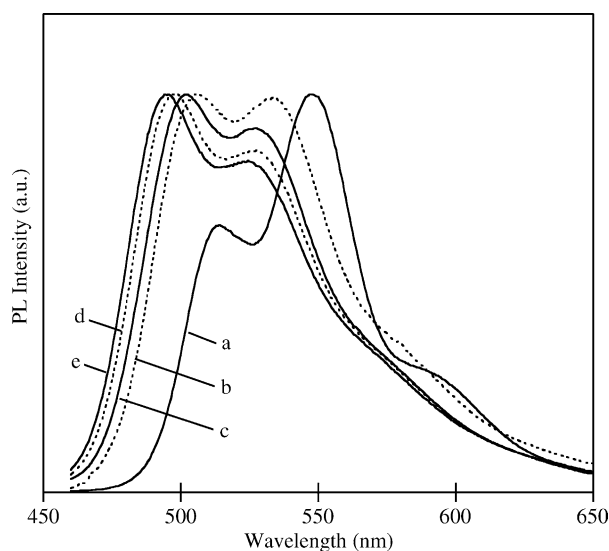


Fig. 4. Photoluminescence spectra of PPV/(20 nm SiO<sub>2</sub>) composite thin films with different particle concentrations: (a) 0; (b) 1; (c) 2; (d) 4; (e) 8%.

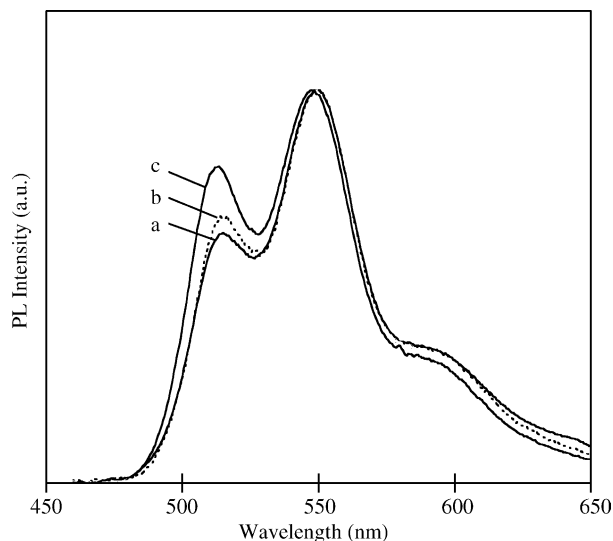


Fig. 5. Photoluminescence spectra of PPV/(20 nm TiO<sub>2</sub>) composite thin films with different particle concentrations: (a) 0; (b) 2; (c) 4%. The spectra of samples with 1 and 8% TiO<sub>2</sub> concentrations are very close to curves (b) and (c), respectively, and are not shown for clarity.

involved in the emission process. Therefore, an increase in intensity of this peak reflects the formation of new segments resulted from a scission of the polymer chains upon introduction of the nanoparticles [17]. This explanation is in agreement with the results obtained from both UV–vis absorption and Raman scattering experiments. The second process to be considered in PPV is the reduction of the film thickness, which also increases the emission of the 515 nm band [19]. This process is compatible with the morphology of the composite thin film, and does not imply a modification of the polymer conjugation length. In fact, when particles are introduced into a polymer film, their spatial repartition will create in the host polymer, thin and small areas, whose thickness decreases with increasing particle concentrations or increasing particle sizes. This explanation is compatible with the evolution of the PL spectra on the concentration and the size of the particles. It does not, however, explain the shifts observed in UV–vis absorption and Raman spectra. It should be noted that from the sole PL point of view, one process does not exclude the other, and considering together all the results in PPV/SiO<sub>2</sub> nanocomposites both processes may occur in these systems.

For the PPV/TiO<sub>2</sub> nanocomposites, the emission bands vary from 550 to 548 nm. The position of the 515 nm band did not change with the increase of the particle concentration but its intensity increases. In addition, as the conjugation length is found to be preserved in these samples from UV–vis absorption and Raman experiments, the enhancement in intensity of the 515 nm band can be assigned to the formation of thin polymer zones in the composite films.

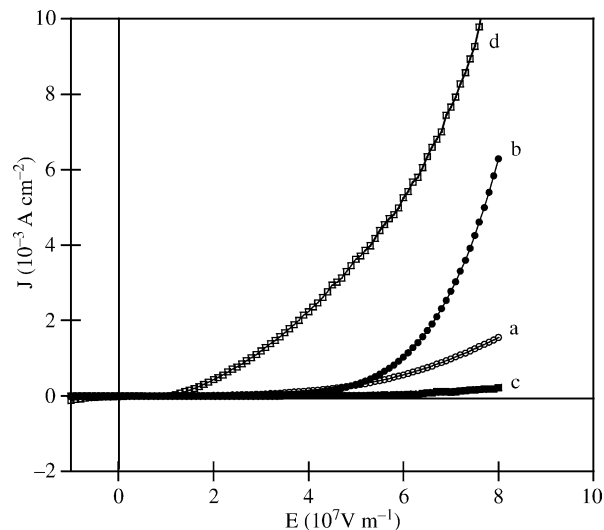


Fig. 6. Current density versus applied field of ITO–composite–MgAg diodes: (a) PPV; (b) PPV/SiO<sub>2</sub> (100 nm, 2%); (c) PPV/SiO<sub>2</sub> (20 nm, 2%); (d) PPV/TiO<sub>2</sub> (20 nm, 2%).

### 3.5. Electrical characteristics of ITO–PPV composite–MgAg devices

Fig. 6 shows the current density versus the applied field for devices using PPV and different composites as an active layer. In devices using PPV/SiO<sub>2</sub> composites, we observe different current variations depending on the particle size. For small size particles (20 nm), the conductivity of the composite decreased with the increasing concentration, while for a larger size (100 nm), it increased with the concentration. A possible explanation for this result is the strong reduction of the polymer conjugation length when using small size particles which alter the intrachain conduction. In contrast, the presence of large size particles in the polymer would favor the interchain conduction by favoring the formation of conducting pathways between the chains.

As for the PPV/TiO<sub>2</sub> composites, the fact that the PPV conjugation length was not changed by incorporation of the particles, suggests that the carrier transport along the polymer chains would not be affected by the oxide. In addition, using an identical particle size (20 nm), we obtained a higher conductivity in PPV/TiO<sub>2</sub> composites than in PPV/SiO<sub>2</sub> ones. Here, the nature of the oxide seems to be at play, and it is possible that the acidic properties of the particles may change charge carrier transport at the contact between the polymer and the particles [20]. However, further investigations using various oxide nanoparticles are needed to elucidate the influence of the nature of the inorganic materials on the conduction mechanisms in composites.

#### 4. Conclusion

In this work, we have investigated the optical and electrical properties of composites made by incorporation of SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles into PPV. We have observed that SiO<sub>2</sub> nanoparticles reduce the conjugation lengths of the polymer, and the reduction is more significant when the particle concentration increases and/or when their size decreases. Incorporation of TiO<sub>2</sub> nanoparticles in PPV did not significantly affect the structure of the polymer, and in contrast, seems to stabilize it by reducing the formation of carbonyl groups. The photoluminescence spectrum of the polymer was modified upon incorporation of the oxide particles with an increase of emission near 515 nm. The electrical characteristics of studied devices showed different variation tendencies depending on the nature and the size of the particles used. Several factors can influence the charge injection into the polymer and their movements inside the composites: the morphology of the contact between the film and the electrode, the dielectric and chemical properties of the particles, and the rupture of the polymer chain length. The use of different kinds of dielectric materials of various sizes and the use of different polymer host matrices would be necessary to fully understand the role of the nanoparticles in these composites.

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