Enhancing the Optical and Optoelectronic Properties of MEH-PPV-Based Light-Emitting Diodes by Adding SiO\textsubscript{2}/TiO\textsubscript{2} Nanocomposites

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A R T I C L E   I N F O

Keywords:
MEH-PPV/(SiO$_2$/TiO$_2$) nanocomposites
optoelectronic properties
charge transfer
dynamic quenching
OLED

A B S T R A C T

The optical and optoelectronic properties of poly [2-methoxy, 5-(2-ethylhexoxy)-1, 4-phenylenevinylene] (MEH-PPV) hybrid thin films containing various amounts of SiO$_2$/TiO$_2$ nanocomposites (STNCs) have been investigated. The solution-blending method was used to prepare all the nanocomposite materials. We found significant quenching of the MEH-PPV emission intensity with increasing STNC content, which results from increasingly efficient charge transfer. The shorter emission lifetimes and decay lifetimes of MEH-PPV/STNCs, in comparison with a pristine MEH-PPV thin film, provide further evidence of efficient charge transfer and also of the absence of static quenching. The purely dynamic quenching in the hybrid thin films is also demonstrated by the absence of any change in the absorption spectrum with increasing STNC content and by the linear Stern–Volmer plot. The efficient charge transfer obtained by increasing the STNC content plays a crucial role in increasing the current and reducing the turn-on voltage of devices, resulting in enhanced OLED performance.

1. Introduction

Recently, conjugated polymers/inorganic hybrid nanocomposites have been employed widely as an active layer to improve the performance of optoelectronic devices such as smart microelectronics, photovoltaic cells, sensors, photodiodes, and light-emitting diodes [1-4]. In devices that use such hybrid layers, when an n-type semiconductor is placed in contact with a p-type polymer, a depletion region of mobile charge carriers is induced at the interface. When photons with energies higher than the bandgap illuminate the polymer, hole-electron pairs are created, which then migrate along the polymer, while electrons are transferred along the nanocrystalline network [5].

A great deal of attention has been focused on the fabrication of optoelectronic devices based on poly (p-phenylene vinylene) (PPV) and its derivatives. In particular, poly [2-methoxy, 5-(2-ethylhexoxy)-1, 4-phenylenevinylene] (MEH-PPV) is one of the most widely investigated of these substances because of its unique electroluminescent properties and particular structure [6]. However, there are significant concerns about the thermal and photo stability of polymers—in addition to other problems associated with polymer-based optoelectronic devices—because they are considered to have poor hole-electron separation and transport properties [7, 8]. Numerous strategies have been suggested to overcome these problems [5-7], but a well-accepted approach is to combine a stable polymer and metal-oxide nanoparticles (NPs)—such as eco-friendly TiO$_2$ or SiO$_2$ NPs—in optimum ratios [6, 9, 10]. Titanium dioxide NPs possess a smaller bandgap and higher refractive index than SiO$_2$ NPs, resulting in stronger scattering. Strong multiple scattering also can be achieved by incorporating TiO$_2$ NPs into the SiO$_2$ NPs [11]. Furthermore, incorporating TiO$_2$ NPs in various ratios significantly affects the structural and optical properties of the SiO$_2$ NPs, as shown in a previous report [12]. Thus, incorporating such nanocomposites into an emitting polymer can play a significant role in improving its optical properties—and thus in the performance of optoelectronic devices fabricated with such polymers—than the addition of either individual TiO$_2$ or SiO$_2$ NPs separately [10, 13].

Despite several reports demonstrating enhancements of the optical and optoelectronic properties of MEH-PPV upon adding individual TiO$_2$ or SiO$_2$ NPs [14-16], there have been no reports on the effects of SiO$_2$/TiO$_2$ nanocomposites (STNCs) on the properties of MEH-PPV. Since the addition of TiO$_2$ or SiO$_2$ NPs individually improves the performance of MEH-PPV-based optoelectronic devices, and since the NPs have better performance in combination, it is believed that such nanocomposites may further enhance the optical properties of MEH-PPV, thus improving photovoltaic applications based on these hybrids as well. The present work is therefore concerned with the effects of various ratios of the STNC content on the optical and optoelectronic properties of MEH-
PPV/STNC hybrid thin films. Here, we report investigations of the effects of STNCs on optical properties such as absorption, the energy gap, the energy-gap tail, photoluminescence, the efficiency of charge transfer, the fluorescence lifetime, and quenching parameters and mechanisms. We have also investigated the effects of STNCs on optoelectronic properties such as the current-voltage characteristics and the turn-on voltage of organic light-emitting diodes (OLEDs). All measurements were carried out at ambient temperature.

2. Materials and methods

We purchased MEH-PPV, with an average molecular mass of 40,000 g/mole, as well as anatase TiO2 NPs from Sigma Aldrich (Saint Louis, Missouri, USA), and we used them as received, without any purification. The sol-gel method was employed to synthesize the amorphous SiO2 NPs and then mixed them with the TiO2 NPs to form homogenous STNCs, as reported previously [12].

The MEH-PPV was dissolved in toluene with the fixed concentration of 5 mg/ml, and STNCs with a weight ratio of 20 wt.% TiO2 was prepared in toluene by the solution-blending method. This method was employed again to prepare the MEH-PPV/STNC hybrids with various weight ratios of STNCs (5, 10, 15, 20, and 30 wt.%). We used glass and indium-tin oxide (ITO) substrates (1.2 cm × 2 cm), on which we deposited 80 μL of each sample by using the spin-coating technique (with the rotation speed and deposition period fixed at 2000 rpm and 20 s, respectively) to form the hybrid thin films for optical and optoelectronic characterization, respectively. The ITO layer served as the anode, and the substrate was etched and patterned by exposing it to HNO3 and HCl vapor at a 3:1 molar ratio. The same process was used to clean both substrates before any deposition, followed by annealing them at 120 °C in a vacuum oven to remove the solvent, as reported in previous work [17]. To fabricate the OLEDs, each ITO substrate with its deposited emissive layer was placed into an electron-beam chamber (at 2.5 × 10−6 Pa) for the deposition of a 150-nm-thick Al cathode at a deposition rate of 2 Å/min. The active area of each OLED device was 0.076 cm2.

An Edinburgh Instrument FLSP920 spectrophotometer was employed to collect both emission spectra and lifetime decays of all samples deposited onto the glass substrates and a Perkin Elmer Lambda 900 ultraviolet–visible spectrometer was used to collect the absorption spectra. Images obtained with a field-emission scanning electron microscope (FE-SEM) provided experimental evidence that the STNCs are well mixed and well distributed with the MEH-PPV. A Keithley 238 measurement system was used to obtain current-voltage measurements of the OLED devices.

3. Results and discussion

Absorption spectra of pristine MEH-PPV and of the MEH-PPV/STNC hybrid thin films are shown in Fig. 1. For pure MEH-PPV, the maximum absorption bands occur at 340 nm and 507 nm, corresponding to the 0-1 and the 0-0 transitions, respectively. In the MEH-PPV/STNC hybrid thin films with different weight ratios of STNCs, the UV-visible absorption peaks occurred at 512 nm. This slight redshift in the 0-0 transition wavelength, together with the slight reduction in broadening of the absorption spectra upon adding the STNCs, suggests that the SiO2 and TiO2 nanoparticles either have no effect on, or only slightly increase, the conjugation lengths of MEH-PPV [18]. However, the 0-0 transition absorbance peak of the thin films was dramatically reduced by the addition of the STNCs, and no additional absorption peak was observed. This confirms the absence of ground-state chemical interactions between the MEH-PPV and the STNCs [19]. In addition, in contrast to the 0-0 transition, the absorbance increased dramatically for the 0-1 transition, showing that the STNCs assisted light harvesting in the UV region of 317–375 nm and that the surface area was increased more than in pristine MEH-PPV.
Using the Tauc equation [20], one can determine the direct and indirect energy gaps for all thin films. The direct ($E_{gd}$) and indirect ($E_{gi}$) energy band gaps were obtained from Figs. 2a and 2b, respectively, and they are listed in Table 1. Upon adding the STNCs, we found only minor decreases in $E_{gd}$ and $E_{gi}$—from 2.159 to 2.136 eV and from 1.982 to 1.944 eV, respectively. The slight decreases in these bandgap values show that the highest occupied molecular orbital and the lowest unoccupied molecular orbital are getting slightly closer to each other [21].

The energy gap tail ($\Delta E$) for all thin films was estimated by using the Urbach plot [22], as shown in Fig. 3 and listed in Table 1. It was noticed that $\Delta E$ increases slightly with increasing STNC content, which we believe to be a result of imperfections in the hybrid nanocomposites. Therefore, the localized density of states within the forbidden gap may have increased, and thus there may be higher degrees of disorder in the electronic structures of the hybrid thin films [23]. On the other hand, the ordered structure of the pristine MEH-PPV results in a reduction in the localized states within the forbidden bandgap and thus a lower value of $\Delta E$ for MEH-PPV [24].

The photoluminescence excitation (PLE) shown in Fig. 4 is centered at $\approx$ 467 nm and 340 nm for pristine MEH-PPV, and this is the case also for the hybrid thin films with added STNCs. The PLE spectra appeared with excitation features at approximately 340 and 467 nm for all samples that exhibit “absorption-like” behavior. This indicates that no significant dimer formation occurred upon adding the STNCs.

Fig. 5 shows the photoluminescence spectra for pristine MEH-PPV and of MEH-PPV/STNC hybrid thin films at an excitation wavelength of 450 nm. Two main emission peaks for pristine MEH-PPV located at 601 nm and 637 nm were observed, which correspond to the 0–0 and the 0–1 transitions, respectively. Both transitions were slightly red shifted—by around 3 to 5 nm—upon adding the STNCs, implying a slight increase in the conjugation lengths of MEH-PPV. Moreover, we observed a dramatic quenching of the intensity with increasing STNC content. We attribute this to efficient charge transfer in the MEH-PPV/STNC hybrids, rather than to energy transfer. Moreover, based on the energy-level positions of the MEH-PPV relative to those of the SiO$_2$ and TiO$_2$ NPs, the separation of excitons at the interface between these materials is energetically allowed, which simplifies efficient charge transfer across the MEH-PPV/STNCs. Efficient charge transfer between the MEH-PPV and the STNCs can be further improved by adjusting important parameters like the Stern–Volmer quenching constant ($k_{SV}$), the fluorescence lifetime ($\tau$) of excited MEH-PPV in the presence of STNCs, the photo-induced electron-transfer rate ($k_{ET}$), and the bimolecular quenching rate ($k_{q}$) [25].

The Stern–Volmer equation, for the simplest case of collisional quenching, can be written as [26]:

$$\frac{I_0}{I} = 1 + k_{SV} [Q],$$

where $I_0$ and $I$ are the emission intensities in the presence and absence of quencher.
of quenching, respectively, and \([Q]\) is the quencher concentration. Since there is no change in the absorption spectrum of the MEH-PPV upon adding the STNCs—and thus no ground-state interactions between the MEH-PPV molecules and the STNCs—the emission quenching is purely dynamic [26]. Moreover, the linear relationship between \(I/I_0\) and \([Q]\) in the Stern–Volmer plot (Fig. 6) gives further evidence of homogeneous quenching (dynamic quenching) in the current hybrid system [27]. The slope of a linear fit to this plot gives the Stern–Volmer constant, \(k_{SV} \approx 166 \, \text{M}^{-1}\). This value implies that 50% of the fluorescence was quenched for an STNC concentration of around 6.02 mM. Moreover, the homogeneous quenching may result from the good distribution of STNCs and also from sufficient coverage of MEH-PPV on the surface of the STNCs, as seen in FE-SEM images (Fig. 7).

In dynamic (purely collisional) quenching, the term \(I/I_0\) can be replaced by \(I_0/\tau\) in the Stern–Volmer equation [26], where \(\tau_0\) and \(\tau\) are the fluorescence lifetimes of MEH-PPV in the absence and presence of quencher STNCs, respectively. The fluorescence lifetime of MEH-PPV was reduced dramatically with increasing quencher (STNC) concentration, as listed in Table 1. All hybrid thin films displayed shorter lifetimes than the pristine MEH-PPV thin film, for which \(\tau_0 = 500 \, \text{ps} [14]\). This also demonstrates both efficient charge transfer [28] and the absence of static quenching for the MEH-PPV/STNCs [14].

The values of \(k_q\) and \(k_{ET}\) for MEH-PPV/STNC hybrid thin films can be calculated by using the following expressions [29, 30]:

\[
k_{ET} = \frac{1}{\tau} - \frac{1}{\tau_0} \quad \text{and} \quad k_{SV} = \tau_0 k_q
\]

(2)

Here the high value of \(k_q, 3.32 \times 10^{11} \, \text{M}^{-1} \cdot \text{s}^{-1}\), demonstrates the good combination between the MEH-PPV and STNCs, because it is significantly greater than the minimum value for efficient quenching, \(1 \times 10^{10} \, \text{M}^{-1} \cdot \text{s}^{-1} [26]\). The calculated values of \(k_{ET}\) (as listed in Table 1) increased gradually from \(0.4 \times 10^6 \) to \(4.4 \times 10^6 \, \text{s}^{-1}\) as more STNCs were added into the MEH-PPV. This finding provides further evidence of significant enhancement in the quenching efficiency, and of charge transfer in the hybrids, with increasing STNC content. In other words, the value of \(k_{ET}\) can be controlled by adjusting the STNC content. A high STNC content results in a high surface area and an increase in defects and thus raises the \(k_{ET}\) values. Thus, highly efficient optoelectrical devices can be fabricated using MEH-PPV/STNC hybrids, as shown below.

The influence of the STNC content on the decay lifetime of MEH-PPV at a collection wavelength of 600 nm—corresponding to the emission region of MEH-PPV—is displayed in Fig. 8 and listed in Table 2. The decay lifetime involves radiative emission, while the calculated fluorescence lifetime in Table 1 involves both radiative and
nonradiative transitions [13, 31]. The presence of one or two lifetimes can be explained by the presence of one or two conformers [32]. Table 2 shows that fast decays are associated with increased quencher content, which results in efficient charge transfer in the hybrids and the presence of dynamic quenching, without any static quenching, as shown above.

The current vs. applied voltage characteristics for OLEDs that use MEH-PPV and MEH-PPV/STNC hybrids as an active layer are shown in Fig. 9. Devices based on MEH-PPV/STNC hybrids produce higher currents and have lower turn-on voltages than those based on pristine MEH-PPV. Moreover, dramatic increases in the current and decreases in the turn-on voltage occur with increasing STNC content, which is in agreement with recent reports of OLED devices based on (PFO/MEH-PPV)/STNCs and MEH-PPV/TiO2 [10, 33]. The enhancement of these electrical properties with increasing STNC content can be interpreted as being due to better injection of charge carriers resulting from the increasing surface area and thus the enlarged interface with the metal electrode [17, 34].

4. Conclusion

This work deals with effects of STNC content on the optical and optoelectronic properties of MEH-PPV. We successfully deposited homogeneous hybrid thin films of MEH-PPV/STNCs on both glass and ITO substrates. As the STNC content increased, the fluorescence intensity and lifetime of MEH-PPV was reduced, suggesting efficient dynamic quenching in the hybrid thin films. We estimated the values of the constants \( K_{SV} \) and \( K_q \) to be about 166 M\(^{-1}\) and 3.32 \times 10^{11} \text{ M}^{-1}\text{S}^{-1}, \) respectively. In addition, the increasing STNC content resulted in a high surface area and an increase in defects, which raised the \( k_{ET} \) values from 0.4 \times 10^6 to 4.4 \times 10^6 \text{ S}^{-1}. \) These findings confirm efficient charge transfer in the hybrids, which plays a crucial role in the performance improvement of OLED devices that employ MEH-PPV/STNCs. This improvement is demonstrated by the increasing device current and reduced turn-on voltage with increasing STNC content in the active layer.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

![Fig. 8. Decay lifetimes, at an emission wavelength of 600 nm, for pristine MEH-PPV and for MEH-PPV/STNC hybrid thin films.](image)

**Table 2**

Main fitting parameters and decay lifetimes of MEH-PPV thin films with various STNC contents. At \( \lambda_{em} = 600 \text{ nm} \).

<table>
<thead>
<tr>
<th>STNCs (wt. %)</th>
<th>Relative amplitude ( B_1 )</th>
<th>( B_2 )</th>
<th>Lifetime (ps) ( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \chi^2 )</th>
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<tr>
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<td>750</td>
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</table>

![Fig. 9. Current-voltage characteristics of OLEDs based on pristine MEH-PPV and the MEH-PPV/STNC hybrid thin films. The inset is schematic structure of the OLED.](image)
Acknowledgement

The authors extend their appreciation to the Deanship for Research & Innovation, "Ministry of Education" in Saudi Arabia for funding this research work through the project number IFKSURG-1440-037.

References