Research Article

Efficient Charge Transfer Mechanism in Polyfluorene/ZnO Nanocomposite Thin Films

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The optical properties and charge transfer mechanism of poly (9,9'-di-cthylfluorenyl-2,7-diyl) (PFO)/ZnO thin films have been investigated. The ZnO nanorods (NRs) were prepared via a microwave technique. The solution blending method was used to prepare the PFO/ZnO nanocomposites. X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM) were used to determine the structural properties, while UV-Vis and photoluminescence (PL) were employed to investigate the optical properties of the films. XRD patterns confirmed that there was no variation in the structure of both PFO and ZnO NRs due to the blending process. FE-SEM micrographs displayed that ZnO NRs were well coated by PFO in all nanocomposite films. The absorption spectra of the nanocomposite thin films exhibited a red-shift indicating the increment in conjugation length of the PFO/ZnO nanocomposite. Significant quenching in the emission intensity of PFO was observed in fluorescence spectra of the nanocomposite films. This quenching was attributed to efficient charge transfer in the PFO/ZnO nanocomposites, which was further supported by the shorter PL lifetime of PFO/ZnO than that of the PFO thin film. The continuous decline in PL intensity of these nanocomposites is attributed to homogenous dynamic quenching between PFO and ZnO NRs.

1. Introduction

The growing interest in polymer-based photoelectric devices, in particular conjugated polymer, can be attributed to several factors such as environmentally friendly, adjustable band gaps, high optical absorption coefficient, and low-cost fabrication. All of these factors can be achieved because of the flexibility in organic synthesis; hence, the chemical tailoring towards the desired properties is possible. For example, poly(3-hexylthiophene) and poly(p-phenylene vinylene) and their derivatives have been reported to absorb light at various wavelengths [1, 2].

There are great concerns about the photo stability and thermal stability of the polymers, although other pressing problems are associated with polymer based photoelectric devices which are poor electron-hole separation and transport properties [3, 4]. While the former concern may be overcome by introducing a more stable polymer, the later problems are more challenging. Several approaches have been suggested to inhibit these problems [5–7], but a well accepted strategy is via hybridization with inorganic semiconducting nanostructures such as metal oxides [8–11]. Successful initial attempts motivate researchers to look for the right combination between a stable polymer and metal oxide and thus their optimum ratio.

In terms of stable polymers, there are a limited number of suitable candidates and one of them is poly[9,9'-di-n-octylfluorenyl-2,7-diyl] (PFO). Earlier work reported that PFO displayed better photo stability and thermal stability than those of the poly(phenylene vinylene)s “PPVs” [12],
which are commonly studied. PFO is a semicrystalline conjugated polymer [13–15] with lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HUMO) of −2.9 and −5.9 eV, respectively [16].

As one of the most widely investigated materials, ZnO is commonly used as electron acceptor in polymer/inorganic nanocomposites [17–20]. This metal oxide exhibits greater tendency to stabilize in wurtzite hexagonal form with conduction band, valence band, and energy gap of −4.2, −7.6, and 3.4 eV, respectively [18]. Most of the earlier works on polymer/ZnO nanocomposites demonstrated the photoluminescence (PL) quenching which was conveniently claimed due to efficient charge transfer effect [17–19].

One of the prerequisites for good photoelectric materials is efficient charge transfer, which in turn depends on the comparable band structures. Benefitting from quantum confinement effect with close consideration on suitability between the band structures, the combination between a more stable PFO and ZnO nanorods (NRs) is believed to result in better materials characteristics for photoelectric application. A common indicator for charge transfer is PL emission quenching. Unfortunately, observation in PL quenching alone is not sufficient to suggest efficient charge transfer. Additional evidence via measuring the fluorescence lifetime is required. However, theoretical approach via calculating fluorescence lifetime [21] is conveniently used as an alternative method especially for researchers having limited equipment at their disposal. The current work is not only calculated fluorescence lifetime, but also other important parameters, namely, the quenching rate constant [22] and photo-induced electron transfer rate [23], which are used together as supplementary evidence to indicate tendencies of determined systems.

Evidence for charge transfer in PFO/ZnO nanocomposites primarily from PL quenching was demonstrated in this work. In addition, values for the aforementioned parameters in case of dry thin films at room temperature were calculated to provide additional evidence for the effective charge transfers. The quenching type and quenching efficiency were also determined in order to have more comprehensive information on the suitability of this nanocomposite as an active layer in the photoelectric devices.

2. Experimental Details

ZnO NRs were synthesized using the microwave technique. A microwave oven (Sanyo Electric model no. EM-G430, 2.45 GHz, 1000 W) was used in this work. Deionized water (resistivity 18.2 MΩ·cm) was used to prepare zinc acetate dihydrate 0.15 M (C\(_6\)H\(_{4}\)O\(_2\)Zn·2H\(_2\)O) (Aldrich, Fluka) aqueous solution (A) and 3.33 M of NaOH aqueous solution (B) at room temperature. The zinc acetate aqueous solution (A) was stirred for 5 min and then the aqueous solution (B) was added dropwise under steady stirring until a white solution was formed. Then, the final white solution was exposed to microwave radiation in the oven for 5 min before being left to cool naturally to 30°C. Subsequently, the solution was centrifuged at 4000 rpm for 5 min to collect the white precipitate produced after radiation. The precipitate was washed with alcohol and deionized water alternately for four times and then was dried under atmosphere at 60°C for 24 h. Finally, the obtained powder was heated at 500°C for 2 h in a conventional oven.

The PFO (product from Sigma Aldrich, USA) with average molecular weight of 58,200 was used in this study. To prepare the nanocomposites, firstly, the PFO was dissolved in tetrahydrofuran (THF) at a concentration of 3.0 mg/mL (PFO/THF). The PFO/ZnO nanocomposites were prepared in solution form by blending the fixed concentration of ZnO (3.0 mg/mL) with various ratios of PFO (0, 10, 30, 50, and 70 wt.%) followed by sonication for 5 min. Then, the solution was deposited onto a glass substrate (1.2 cm × 2 cm) to form three layers by a spin coating technique (rotational speed of 2000 rpm for 30 s). Finally, it was left to dry at room temperature.

The structural characterization of the films was carried out by X-ray diffraction (Bruker-AXS D8 Advance X-ray diffractometer using Cu-K\(_{α}\) radiation source with λ = 1.5418 Å). The nanostructure of the films was observed using a field emission scanning electron microscope (FE-SEM) model Supra 55VP with operating voltage of 3.00 kV. The absorption and emission spectra of the films were recorded using UV-Vis spectrophotometer (Perkin Elmer LAMBDA 900) and Luminescence spectrometer (Perkin Elmer LS55), respectively.

3. Results and Discussion

The X-ray diffractograms for the ZnO NRs, PFO, and PFO/ZnO nanocomposite thin films are shown in Figure 1. The diffractogram of ZnO NRs shows that all peaks can be indexed to the wurtzite hexagonal structure of ZnO crystal and no other crystalline peaks of any impurities were detected (Figure 1(a)). By comparison, the XRD diffractograms for PFO consist of a narrow peak at 7° and broad peaks in between 10° and 30° (2θ), which can be deconvoluted into three broad peaks at 15.5°, 20.0°, and 23.1°. This observation confirmed that the PFO is in semicrystalline phase as suggested by earlier reports [13–15]. The X-ray diffractograms for nanocomposite thin films consist of broad PFO peaks with several narrow peaks representing ZnO NRs. The intensities of ZnO NRs peaks in these nanocomposite films are enhanced as more ZnO NRs are added into the polymer (Figure 1(c)). More importantly, the structure of both PFO and ZnO NRs remained unchanged even after the blending process.

Figure 2 displays the morphology of ZnO NRs and PFO/ZnO nanocomposites. The ZnO existed as wurtzite hexagonal nanorods (pencil-like) having an average diameter of about 95 nm and length of 800 nm (Figure 2(a)). The nanorods were closely packed which were grown from a common seed. The smooth hexagonal structures of the ZnO NRs confirm that the nanorods were well crystalline as wurtzite unit cell.

The general view of nanocomposite film (Figure 2(b)) reveals the uniformity of the deposited film. A closer view of
the films showed that the majority of ZnO NRs were broken into smaller rods and covered by PFO in all nanocomposites thin films (Figures 2(c)–2(f)). At 10 wt.% ZnO NRs, all nanorods were covered and uniformly distributed. As the ZnO NRs content increased, the nanorods were thinly coated by the PFO. At 70 wt.%, there were many uncoated nanorod bundles, which are believed to be due to the lack of PFO.

The absorption spectra of all films were presented in Figure 3. The UV-Vis spectrum of PFO film displays a $\lambda_{\text{max}}$ at 404 nm which corresponds to a $\Pi-\Pi^*$ transition [24] and a shoulder around 435 nm as the fingerprint for $\beta$-phase of PFO [25]. By comparison, the absorption edge of ZnO NRs was located in the UV region (<360 nm), which is similar to an earlier report [21]. Upon addition of ZnO NRs, the absorbance of the nanocomposite films was dramatically reduced. No additional absorption peak was observed in the spectra confirming the absence of interaction between PFO and ZnO NRs at the ground states [19].

Relative to pure PFO, all absorption peaks of PFO/ZnO nanocomposite thin films were red-shifted (around 11 nm) signifying the extension in the conjugation length of the nanocomposites [26–28].

Figure 4 shows the fluorescence spectra of ZnO NRs, pure PFO, and PFO/ZnO nanocomposite thin films with various ZnO contents. The UV emission in the fluorescence spectrum of ZnO NRs (Figure 4(a)) comprises two overlapping bands. The peak of the first band centered at 378 nm, which is related to the near-band edge emission of the wide band gap ZnO NRs. This band was due to the recombination of excitonic centres in the nanorod [29]. Additionally, a broad green band at 460–550 nm was observed, which is mainly caused by the intrinsic defects or oxygen vacancies in the ZnO NRs and results in the recombination of a photo-generated hole with the single ionized charge state of this defect [21, 30].

Figure 4(b) reveals the emission peaks of PFO at 427, 442, 465, and 500 nm, which were assigned to 0–0, 0–1, 0–2, and 0–3 vibronic transition, respectively. As in absorption spectra, addition of ZnO NRs resulted in red-shift of the emission peaks position. More importantly, a dramatic quenching of PFO emission intensity was observed, and above 30 wt.% of

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**Figure 1:** XRD patterns of (a) ZnO NRs, (b) pure PFO, and (c) PFO/ZnO nanocomposite films.
ZnO NRs content, the 427 nm peak of pure PFO completely disappeared.

Since there was no overlap between the emission spectrum of PFO (Figure 4(b)) and the absorption spectrum of ZnO NRs (Figure 3(a)), dramatic PL quenching in PFO in the hybrid system was due to charge transfer from the polymer to the metal oxide NRs [31]. Due to the presence of ZnO NRs, recombination of exciton in PFO was inhibited. Instead, the electron-hole pairs in the polymer dissociated at the PFO/ZnO interface with the electrons moving across the interface into ZnO NRs while the holes remain in the PFO.

This argument is supported by the fact that the conduction and valence bands of ZnO are relatively lower than those of PFO. Therefore, from an energy level point of
Figure 3: Absorption spectra of PFO/ZnO nanocomposite films.

Figure 4: Fluorescence spectra of (a) pure ZnO NRs, excitation at 320 nm, and (b) pure PFO and PFO/ZnO nanocomposite films, excitation at 355 nm.

Figure 5: The interfacial charge generation, transfer, and separation between PFO and ZnO NRs. (Open circle: hole; closed circle: electron).
The bimolecular quenching rate ($k_q$) and the photo-induced electron transfer rate ($K_{ET}$) for PFO/ZnO nanocomposite films can be calculated using (2) [33] and (3) [34] as follows:

$$K_{SV} = \frac{\tau_0}{\tau} = 1 + K_{SV} [Q],$$

$$K_{ET} = \frac{1}{\tau - \frac{1}{\tau_0}}.$$  

Using (2), the $k_q$ has been evaluated as $5.59 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}$. This value is significantly greater than the minimum value for efficient quenching, which is $1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ [22]. The high value of $k_q$ obtained in this work proves the good combination between the ZnO NRs and PFO. Equally important, high $k_q$ value signified the admirable quality of the interface between these two materials. The values of $K_{ET}$ calculated using (3) were constantly increased from $1.53 \times 10^9$ to $12.73 \times 10^9 \text{ S}^{-1}$ as more ZnO NRs are added into PFO (Table 1). This finding provides additional evidence illustrating significant improvement in quenching efficiency and charge transfer in PFO/ZnO nanocomposite upon increment of ZnO NRs. The calculated $k_{ET}$ values in this work are comparable with other organic-metal oxide nanocomposite systems such as phycocyanin/TiO$_2$ [23]. In other words, the photo-induced electron transfer rate from PFO monomers to ZnO NRs can be controlled with the ZnO NRs content. High ZnO NRs content has a high surface area, which gives an increase to a lot of defects and raises the electron transfer rate. Consequently, more efficient PFO/ZnO nanocomposite can be obtained as an active layer in photoelectric devices.

4. Conclusion

This work reports on the study of charge transfer mechanism in PFO/ZnO nanocomposite thin films. ZnO NRs were successfully synthesized using the microwave technique, whereas PFO/ZnO nanocomposites were successfully prepared via solution blending method prior to producing the films using spin coating technique. The X-ray diffractograms confirmed the purity of ZnO NRs and the existence of amorphous phase of PFO and crystalline phase of ZnO NRs. As the ZnO NRs content increased, the emission intensity of PFO reduced suggesting enhanced quenching fluorescence of PFO. The quenching rate ($K_{SV}$) and the bimolecular quenching rate ($K_{ET}$) constants were estimated to be about $193.27 \text{ M}^{-1}$ and $5.59 \times 10^{11} \text{ M}^{-1} \text{S}^{-1}$, respectively. In addition, as the ZnO NRs content increased from 10 to 70 wt.%, the photo-induced electron transport rate increased from $1.53 \times 10^9$ to 12.73 x $10^9 \text{ S}^{-1}$. Moreover, it was found that the photoluminescence lifetime for the PFO/ZnO thin films is much shorter than that of the pure PFO thin film. These findings confirmed the efficient electron transfer across PFO/ZnO interface, which are very crucial for greater improvement in the performance of the PFO/ZnO based photoelectric devices.
Table 1: Photo-induced electron transport rate and lifetime values of PFO/ZnO nanocomposite thin films.

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<thead>
<tr>
<th>The weight ratio of ZnO NRs (wt.%)</th>
<th>Concentration of ZnO NRs [Q] (mM)</th>
<th>Lifetime of PFO ( \tau ) (ns)</th>
<th>Photo-induced electron transport rate ( k_{ET} ) (S(^{-1}) ) ( \times 10^9 )</th>
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<tr>
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Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

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References


