FACILE PREPARATION OF P3HT–ZnO HETEROSTRUCTURE: STRUCTURAL AND SPECTROSCOPIC PROPERTIES

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Abstract

In the current research work we demonstrate the ability to enhance the absorption properties of poly(3-hexylthiophene) (P3HT) via ZnO nanocrystals doping. Structural properties, optical absorption and vibrational modes of the samples were probed by means of X-ray diffraction (XRD), Ultraviolet–Visible (UV–Vis) spectroscopy, Raman spectroscopy and Fourier Transform InfraRed (FTIR) Spectroscopy. The effectiveenhancement of the absorption characteristics reveals that P3HT–ZnO heterostructure is an outstanding candidate for efficient hybrid photovoltaic (HPV) applications.

1. Introduction

Over the past decade conjugated polymer such as P3HT have stimulated much attention in the scientific community owing to its attractive structural, optical and electrical properties which are of considerable interest in the development of efficient low-cost optoelectronic devices such as solar cells, gas sensors, photodetectors, organic field-effect transistors (OFETs), etc [1 – 4].

Recently the inorganic-organic structures have gained momentum in the development of efficient low-cost bulk heterojunction (BHJ) hybrid photovoltaic devices. Several heterostructures of interest are possible among which those based on Fe_2O_3, CdSe, PbS, TiO_2, CdS and ZnO semiconductors, just to cite few [5 – 10]. Due to the fact that some of the commonly used semiconductors are disadvantageous at some extent, ZnO appear to be the most promising alternative owing to its outstanding characteristics such as low-cost, non-toxic, low crystallization temperature, etc [11].

The current study focuses on the synthesis of a promising hybrid semiconductor material which has not been extensively investigated so far. Since the inception of the concept of organic-inorganic hybrid solar cells, only few works to the best of our knowledge have been reported on the enhancement of optical absorption properties of ZnO nanocrystals doped P3HT nanocomposite [12, 13]. Overall, in this report we demonstrate a systematic harvesting of light absorption induced by ZnO nanocrystals in P3HT which was prepared via a direct solution mixing procedure.

2. Experimental

The ZnO nanocrystals powder used in the current study was synthesized following the procedure described in our previous works [14, 15]. In a typical procedure ZnO nanocrystals powder was dissolved in absolute ethanol via a systematic sonication for 15 min at room temperature to obtain a clear aqueous ZnO solution (S1). On the other hand, P3HT solution was obtained by dissolving poly(3-hexylthiophene-2,5-diyl) in chlorobenzene (solvent) under rigorous stirring for 2 h at 40 °C. The resulting yellowish solution (S2) of P3HT (0.54 mg / ml) was then used to fabricate the reference film (F1) and further mixed to the ZnO solution for the fabrication of the P3HT–ZnO film (F2). To form P3HT–ZnO solution, S1 and S2 were mixed and stirred for 30 min resulting in a bluish-dark solution (S3). At the same time the glass slides were rigorously cleaned in successive acetone and alcoholic solution several times under constant sonication for 30 min. To fabricate the films, S2 and S3 were respectively deposited on pre-heated glass slides by drop casting process and allowed to dry in air for 48 hours in the dark. XRD measurements were carried out on RigakuSmartlab diffractometer using Cu Kα radiation (λ=0.1540593 nm) using a 45 kV tube voltage and 200 mA tube current (X-ray generator parameters). The experiment was carried out using the out-of-plane and in-plane 1D grazing incidence XRD mode. The room temperature (RT) UV–Vis absorption spectra of the P3HT and P3HT-ZnO films were investigated using a Perkin–ElmerLambda 1050 UV / Vis / NIR spectrophotometer equipped with integrated sphere. Raman scattering were collected using a Horiba Jobin-Yvon HR800 Raman spectrometer equipped with a visible microscope with a 514 nm excitation Ar^{+} laser with a spectral resolution of 0.4 cm^{-1} at RT. Fourier transform infrared (FTIR) spectra were collected at RT in the transmittance mode using a Perkin–Elmer 100 FTIR spectrometer.

3. Results and discussion

Figure 1 depicts grazing incidence X-ray diffraction (GIXRD) patterns of the as-prepared films. Three intense diffraction peaks at 2θ = 5.48, 19 and 23 ° of the patterns were assigned to (100), (010)′ and (010) crystallographic reflexions of P3HT. The most prominent (010) diffraction peak is associated with the π–π* stacking of the polythiophene backbones [16]. However, the additional reflexions observed at 2θ = 31, 34, 36 ° correspond to the hexagonal wurtzite structure of ZnO (see **Figure 1a**). More importantly, the change in scanning orientation from out-of-plane to in-plane revealed a systematic change of the structure crystallinity which may be related to the different lattice orientations exhibited by P3HT and ZnO.

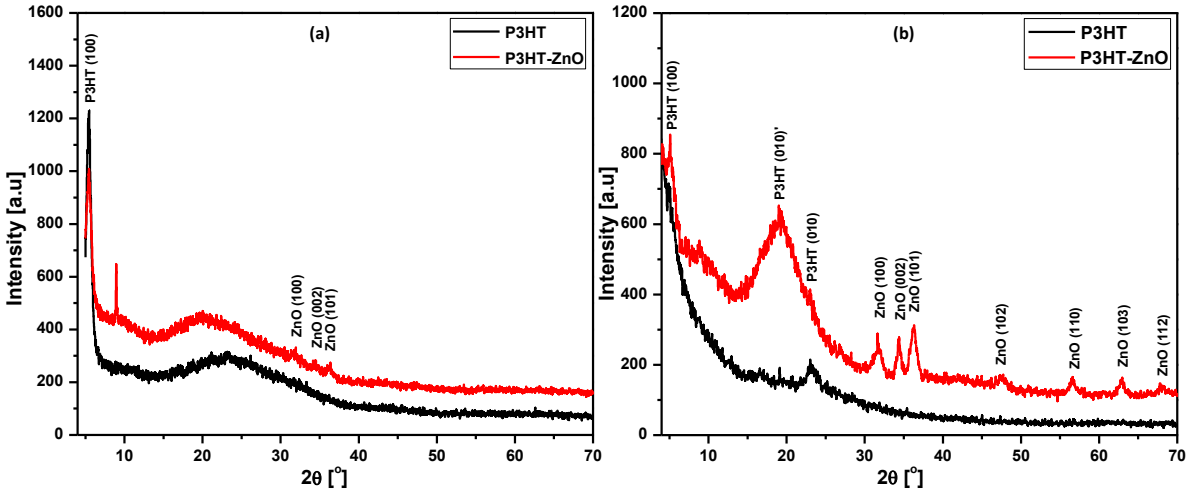

Figure 1. Out-of-plane (a) and in-plane (b) GIXRD patterns of the prepared samples.

Figure 2 shows typical broad absorption spectra ranging from 350 – 750 nm of P3HT due to intermolecular π–π* ordering. There was a distinguished enhancement of the absorption spectra of doped as compared to un-doped P3HT film, implying effective improved photo generated exciton due to ZnO doping. Moreover, the slight red shift observed in the doped π-π* spectrum edge denotes a reduced band gap due to enhanced electron delocalization being assigned to charge transfer [17, 18]. The resulting graded of the band gap which may lead to the broadening of the absorption spectrum of the doped P3HT film suggest a good match with the solar irradiance spectrum as compared to the P3HT film.

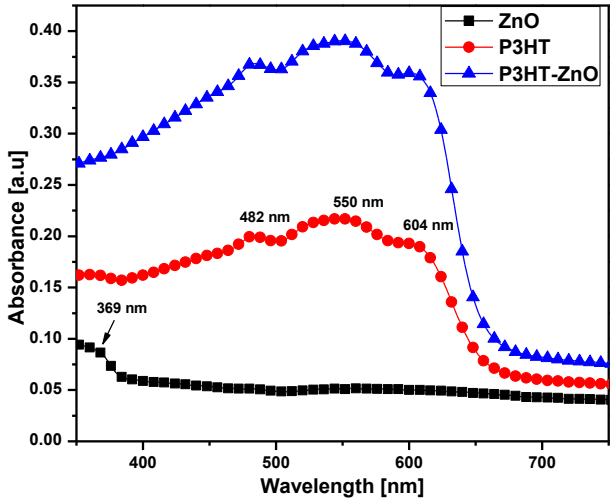

Figure 2.UV–Vis absorption spectra of the samples.

Figure 3 shows Raman scattering spectra recorded for P3HT and P3HT–ZnO films. Various Raman characteristic peaks were observed in the scattering spectrum. The most prominent Raman band was observed at about 1447.3 cm^{-1} which was associated with a less intense peak at 1379.4 cm^{-1}, the peaks were assigned to the C=C stretching vibrations of thiophene ring and C–C skeletal stretching vibrations [19, 20]. Moreover, the band at about 598.8 cm^{-1} was assigned to in-plane thiophene ring deformation. Furthermore, the peaks observed at 675 and 725.4 cm^{-1} were assigned to the symmetric and antisymmetric C–S–C deformation vibrations on the thiophene ring, respectively, while the peak at about 873 cm^{-1} was due to C–H out-of-plane deformation. Finally, the peaks located at about 2827 and 289 cm^{-1} correspond to the C–H symmetric and antisymmetric stretching, respectively.

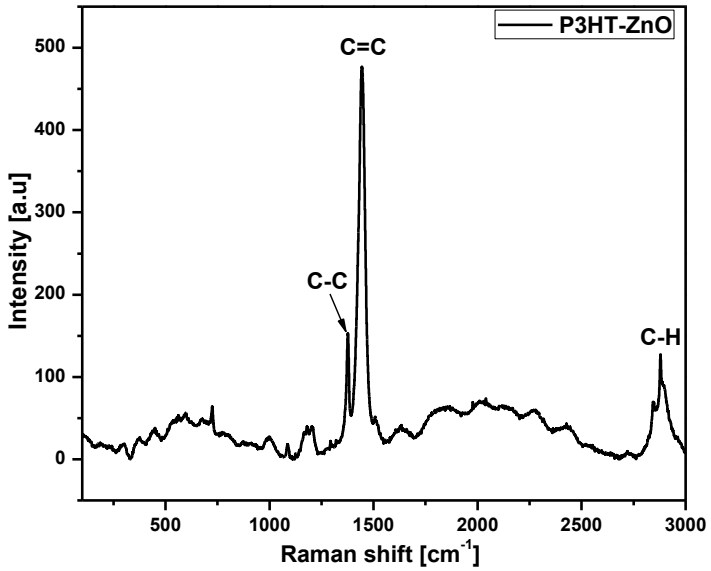

Figure 3.Raman scattering spectra of P3HT–ZnO film.

Figure 4 shows the FTIR spectra of P3HT and P3HT–ZnO films. The spectra look similar with slight differences mostly related to the intensities of the absorption peaks which is most pronounced in the P3HT–ZnO film. However, both spectra exhibited two main bands at about 3030 cm^{-1} and 2931 – 2847 cm^{-1} which are respectively due to C=CH and stretching vibrations of C–H bonds on the thiophene ring. Moreover, the broad absorption band in the range of 3300 – 3500 cm^{-1} was ascribed to ≡C–H bonds [19].

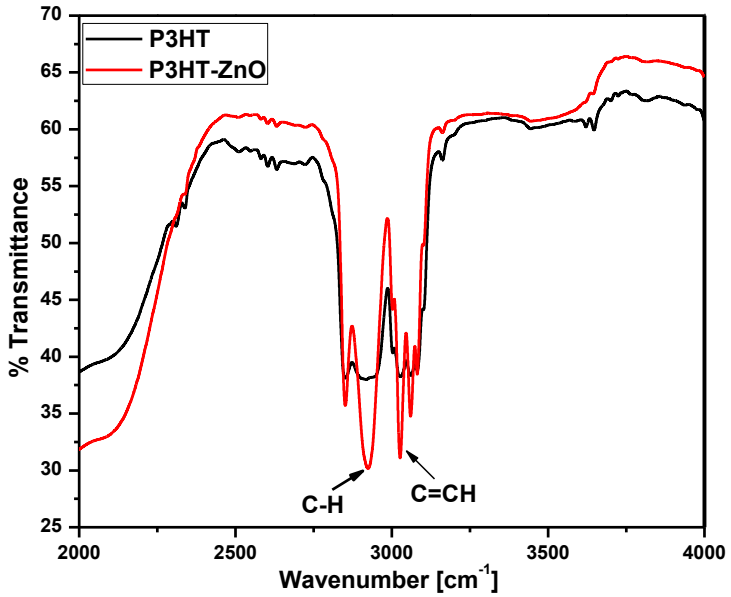

Figure 4.FTIR spectra for P3HT and P3HT–ZnO films.

4. Conclusion

In the current research work we have successfully prepared a hybrid material for solar cell active layers via a direct solution mixing procedure. The obtained enhanced absorption characteristic due to improved photoinduced charge transfer between the organic and inorganic semiconductors is paving the way to potential high efficient and low-cost hybrid optoelectronic devices.

Acknowledgements

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