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Bulk heterojunction photodiode: To detect the whole visible spectrum

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ABSTRACT

In this paper, we report an organic bulk heterojunction photo-sensor that has been fabricated by using a composite of a polymer material poly(3-hexylthiophene-2,5-diyl) (P3HT) and a dye material vanadyl-phthalocyanine (VOPcPhO). The UV–Vis spectrum shows that this composite exhibits a broad absorption over the whole visible range. The photoluminescence (PL) spectra of P3HT and VOPcPhO blend have been studied to optimize the ratio of P3HT and VOPcPhO. The photo-sensitivity has been investigated under different applied voltages in reverse direction. The photoconductivity sensitivity value has been calculated as 5.65×10^2 Sm/W. The photo-responsivity of the sensor has been investigated under 100 mW/cm^2 illumination. It is found that the sensor exhibits a rapid change in the photocurrent by the switching of the light between ON and OFF states and shows stable plateau values. Since this new photo-sensor device can harvest photons over the whole visible range and is inexpensive to manufacture, therefore, it has a great potential for practical applications.

1. Introduction

Sensor applications have significantly contributed to more efficient use of resources and thus reduce the sources of pollution and other greenhouse-gas emissions [1]. As far as the materials for sensor applications are concerned, organic semiconductor materials have attracted researchers since the last decade for their interesting properties and environmentally friendly manufacturing processes. Furthermore, the high sensitivity of organic semiconductor materials to the ambient conditions is also a major reason that makes them very promising for development for various types of sensors [2–4].

For the last few years, the bulk heterojunction concept appeared as the most efficient organic semiconductor idea with respect to processing costs and has been considered as a dominant design for organic photodiodes and solar cells [5–8]. It has been reported by Sayhan et al. that the use of polymer material together with an organic dye content enhances the harvesting of photons from light [9]. The study of a polymer-dye device in the form of a thin film by Honda et al. [10] has revealed proficient light harvesting by both dye and polymer components. This device consists of a donor–acceptor blended structure with a dye component selectively localized between the heterojunction interfaces. The photocurrent was increased by the addition of dye material which was capable of collecting more photons in the spectrum region where the donor and acceptor blend cannot efficiently harvest. These investigations prove that the employment of a dye material is to achieve a high photo-conversion as the photocurrent of the device increases due to direct photo-excitation [11].

Among the organic dyes, phthalocyanines are the heterocyclic macrocyclic organic compounds. Phthalocyanines molecules are fully conjugated, containing a π-electron system [12]. This conjugated system is responsible for their high sensitivity [13]. The new combination of donor-blended system is introduced in this work, consisting of regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) and

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vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOPcPhO). The introduction of this VOPcPhO in P3HT matrix is to encounter the limitation of a big fraction of the solar spectrum absorption. The composition of this blend system has not been reported as yet. In this study, we investigate the contribution of VOPcPhO content and the influence of different P3HT:VOPcPhO compositions of the blended system. The aim of this work is to introduce a novel blended system that can open the way to the development of a highly sensitive photo-sensor to cover the whole visible range.

2. Experimental

Poly(3-hexylthiophene-2,5-diyl) (P3HT) and vanadyl-phthalocyanine (VOPcPhO) were purchased from Sigma–Aldrich. Molecular structures of P3HT and VOPcPhO are shown in Fig. 1. P3HT and VOPcPhO were dissolved using chloroform to make 20 mg/mL and then mixed within three different volume ratios (1.0:1.0, 1.0:1.5 and 1.0:2.0). ITO-coated glass substrates were cleaned using acetone, isopropyl alcohol, and de-ionized water and subsequently dried through blown Nitrogen prior to the PEDOT:PSS deposition. The 40 nm thick PEDOT:PSS film was deposited using a spin coater. The PEDOT:PSS films were annealed at 120 °C for 10 min. The P3HT:VOPcPhO blended solutions was spin coated on PEDOT:PSS layer to deposit 150 nm thick film followed by annealing at 120 °C for 30 min. Finally, the top Al electrodes (2 mm diameter) were deposited by means of thermal evaporation under vacuum conditions. The fabricated ITO/PEDOT:PSS/blend/Al devices were post annealed at 120 °C for 30 min before it was further characterized. The absorption spectra were recorded using a UV–Vis–NIR spectrophotometer (Shimadzu UV-3101PC). Photoluminescence (PL) measurements were performed using RENISHAW inVia Raman Microscope using a 325 nm wavelength laser source. Electrical characteristics of the sensor were performed using a computer interfaced (Keithley) source measuring unit (SMU) and the Oriel 67005 solar simulator was used as a light source. The intensity of light irradiant was varied from 40 mW/cm^2 to 140 mW/cm^2 and the calibration was done by using a power meter (Newport model 1815-C). The characterization was carried out under ambient conditions at room temperature. The electrical measurements presented here were performed on the samples after three weeks aging in an open environment to allow it fully degrade.

3. Results and discussion

The absorption spectra of the P3HT:VOPcPhO composite thin films with different volume ratios are shown in Fig. 2. Both the P3HT and VOPcPhO components lie in the range 450–750 nm of the visible spectral region. However, the spectral range of absorption for each single component is limited but when combined together, these materials are well suited for light applications. The high-energy peak for P3HT exists at 518 nm with two shoulders at 550 nm and 600 nm. No absorption can take place beyond 650 nm in P3HT. Therefore, it seems feasible to add VOPcPhO to extend the absorption to longer wavelengths in the red region. The absorption spectrum of VOPcPhO shows the main absorption at 665 nm and 715 nm (Q-band) besides the characteristic Soret absorption bands are in the region of 300–500 nm. The VOPcPhO is perfectly suited to extend the absorption spectrum to a longer wavelength. The blended film exhibits the absorption spectrum which includes features of the two components P3HT and VOPcPhO. The broad absorption spectrum may contribute to greater light harvesting and is capable of absorbing at longer wavelengths without diminishing the shorter wavelength absorption.

The photoluminescence (PL) of P3HT and VOPcPhO blend have been studied to optimize the ratio of P3HT and VOPcPhO for further investigations for photo sensors. The inset in Fig. 2 shows the PL spectra of the blend of P3HT:VOPcPhO measured at room temperature. The PL spectra of the thin films and their blends were obtained by an excitation wavelength of 325 nm in the range from 400 to 1000 nm. It is evident from Fig. 2 that when P3HT and VOPcPhO are in a matrix with volume ratio 1.0:1.5, the intense PL of the blend is significantly quenched and red shifted. The photoluminescence quenching indicates that the photo-induced charge transfer in the P3HT:VOPcPhO (1.0:1.5) blended film is much better than the rest of the ratios and this ratio is selected for the fabrication of the photo sensor.

The electrical characteristics of the ITO/PEDOT:PSS/P3HT:VOPcPhO/Al light sensors were measured under different illuminations. Fig. 3 shows that the photocurrent of the P3HT/VOPcPhO composite is considerably enhanced as the illumination increases. The same trend is observed when the photocurrent was measured under different applied biasing. As the biasing increases, the sensitivity of the sensor also increases. The reverse biased current–voltage characteristic has moved in the negative (-ve) direction

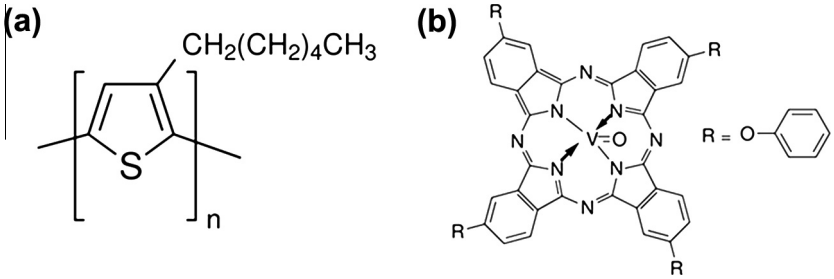

Fig. 1. Molecular structure of: (a) poly(3-hexylthiophene-2,5-diyl) regioregular (P3HT) and (b) vanadyl-phthalocyanine (VOPcPhO).