Plasmon resonance in photoactive P-N junction blend, spin coated from self-made low cost spin coating machine for plastic solar cell

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Abstract

In the present work, spin coated thin films of P3HT: NTCDA donor- acceptor blends of weight ratios 3:1, 1:1 ,1:3 are prepared in Toluene using the self-made spin coating machine. The experiment is focused to optimize the P:N weight ratio of the photoactive blend that can absorb maximum solar energy and also to enhance the absorption by doping it with gold nano particles. Absorption property of the samples are studied using JASCO UV VIS 670 spectrometer which shows that 1:3 blend has the broad spectral response and considered to be the best active blend. The optical band gaps of the samples are determined through Tauc's plot, wherein the onset wavelength for 1:3 sample is found to be 660nm with a band gap of 1.87 eV. The optimized 1:3 blend is doped with gold nano-particle dispersion in citrate buffer. The absorbance gets increased on doping with nano particle with extremely broadened spectral response which is attributed to the Localized Surface Plasmon Resonance(LSPR). Photons are trapped by the gold particles in the polymer matrix for the efficient harvesting of the solar energy. The construction of the solar cell using this Plasmon enhanced photoactive material is the work under progress. Copyright © 2017 VBRI Press.

Keywords: P3HT, PCBM, NTCDA, Plasmon Resonance, polymer composite.

Introduction

The first-generation silicon based cells and even the second-generation thin film solar cells suffer from material cost, installation cost and fabrication complications [**1**]. Organic solar cells are promising because of their low cost, simple processing, flexibility, tunability and light weight. Low efficiency being the main drawback of these solar cells, the search for an efficient, stable organic solar cell is the most challenged and demanded research problem [**2**]. In the constructional hierarchy, single layer, bi-layer, bulk hetero-junction, tandem cells & Plasmon enhanced cells follow in steps in an attempt to achieve more efficiency. The main difficulty with plastic solar cells is the electron – hole recombination before the exciton migration to the P-N junction interface. The problem is overcome by introducing the concept of bulk hetero junction blend of donor-acceptor pair. Due to the formation of numerous P-N junctions in the blend, the excitons can easily encounter the junction interfaces to get separated as charge carriers. This bulk hetero junction concept of the donor- acceptor system has proved remarkable progress in the efficiency enhancement.

The donor- acceptor system has proved remarkable progress in the efficiency enhancement through the effective exciton diffusion mechanism and the charge collection rate but the blend must be properly tuned with respect to the choice of donor-acceptor pair as well as their weight percentage ratio to have a broad solar spectral response. Among the conducting polymers, P3HT has the absorption spectrum matching well with the strongest solar spectrum and also has good transport properties.

The work is focused to prepare an optimized active blend of the widely-used donor polymer Poly [3-hexylthiophene-2, 5-dily) (P3HT) and the N-type acceptor 1, 4, 5, 8 Naphthalene tetra carboxylicdianhydride (NTCDA), The strong absorption spectrum of P3HT in the visible region and the prominent absorption of NTCDA in UV region along with the broad tail of absorption beyond the visible region are the key factors in selecting them as the blend pair. The resulting active blend must show a broad spectral absorption for a proper composition between them. Blends of different donor-acceptor weight ratios are prepared in high boiling point solvent Toluene and their glass coated samples (Spin Coating) are characterized by UV-Visible spectra. The

blend showing broad spectral sensitivity for absorption is selected as the best photo active blend. Optimized blend is doped again with gold nano-particles by which the absorbance has been enhanced.

Experimental

Materials

The p-type donor Poly[3-hexylthiophene-2,5-dily) (P3HT) (grade -electronic grade, average mol.wt –15000 to 45000, melting point – 238°C, HOMO --5eV, LUMO --- 3e V, energy gap (E_g) 2eV, solubility-chloroform, trichlorobenzene, chlorobenzene, toluene and Xylene, P type mobility-- $10^{-4} – 10^{-1}$ cm^2/V-s) were purchased, the n-type acceptor 1, 4, 5, 8- Naphthalen tetra carboxylic dianhydride (NTCDA) (melting point is greater than 300°C , N type mobility 0.003 cm^2/V-s) and the Gold nano particles (contains Proprietary Surfactant as concentration ~6.0X10^{12} particles / mL OD1 absorption - λ_{max} 510-525 nm) of size 10 nm diameter are purchased from Sigma Aldrich Corporation, The solvent Toluene is procured from Rankem Chemicals India. These chemicals are used as received without further purification. The chemical structures of these donor and acceptor molecules are as shown below.

P3HT   **NTCDA**
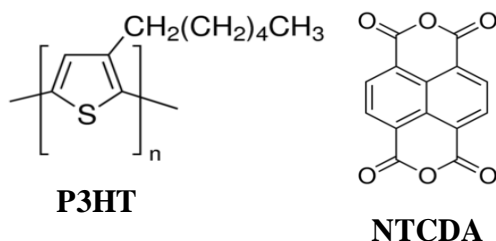
Processing method

30 mg of P3HT and NTCDA are dissolved in 65 CC and 40 CC of Toluene respectively in separate beakers and magnetically stirred for 48 hrs at room temperature until clear solutions are formed. The resulting solutions are of concentrations 0.46 mg/cc and 0.75mg/cc. The solutions are blended with P3HT: NTCDA weight ratios of 3:1, 1:1 & 1:3 keeping the total weight of the film at 5 mg. The mixtures are magnetically stirred for 3 days at room temperature and then spin coated on glass substrate, dried at room temperature and then at about 50° C in hot air oven. The film composition is as shown in the table below.

Results and discussion

Major problem in polymer solar cells is the insufficient absorption in the solar irradiance spectrum. Even the widely studied Phenylene vinylene polymers have the band edges at 550nm. **Fig. 1(a)** represents the absorption of pure P3HT spin coated film indicating the absorption extending from 300 nm to 634 nm. The Spectrum has two peaks at 520nm and 560 nm arising from $\pi - \pi*$ transition and the shoulder at 620nm is due to inter-chain interactions [3, 4]. The onset of absorption (absorption edge) is 634nm so that the absorption spectrum of

pure P3HT is matching well with the strongest solar spectrum. The N type material 1,4,5, 8-naphthalene-tetracaboxylicdianhydride (NTCDA) is planar π-stacking organic molecule which is an excellent model compound for optoelectronic organic semiconductor thin films, particularly organic diodes. The molecule has a naphthalene core NTCDA with a delocalized π electron system and two anhydride terminal groups. NTCDA is an acceptor and well known for high spectral selective absorption with good semiconducting property.

Table 1: Sample Composition.

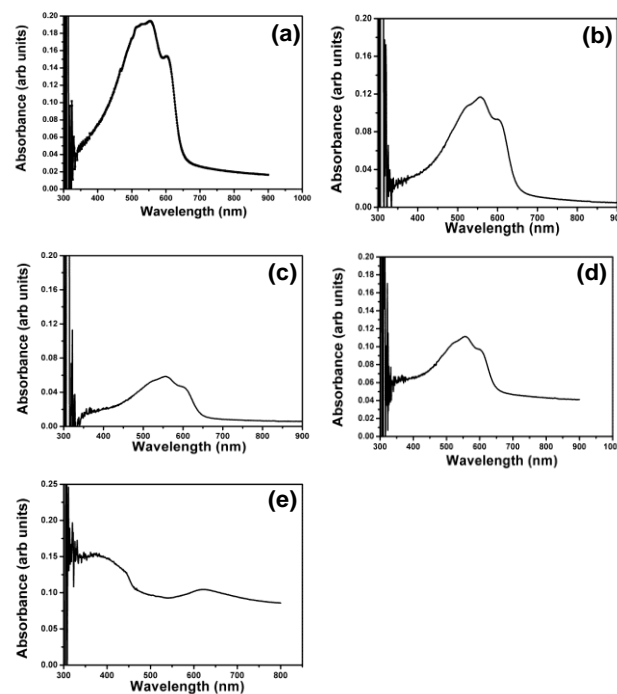| P3HT/Toluene (P type)	NTCDA/Toluene (N type)	P:N
5mg (10.86cc)	-----	Pure p
3.75mg (8.15cc)	1.25mg (1.66cc)	3:1
2.5mg (5.43cc)	2.5mg (5.33cc)	1:1
1.25mg (2.71cc)	3.75mg (5cc)	1:3
....	5mg(6-66cc)	Pure N

Fig. 1. Absorbance spectra of (a) Pure P, (b) 3:1 P:N (c) 1:1 P:N (d)1:3 P:N (e) pure N.

It is a highly conjugated system with broad band of absorption with selective peaks between 400nm to 600nm Addition of NTCDA into P3HT polymer matrix generates multiple donor-acceptor P-N junctions assisting ease exciton migration and improved charge collection [**5,6**]. **Figs. 1(b, c, d)** are the absorption spectra for 3:1,1:1 and 1:3 P3HT:N TCDA blends. Important features can be outlined from the overlay shown in **Fig. 2**. Relatively 1:3 blend has wide spectral sensitivity and can be considered as the best photoactive blend among the samples prepared.
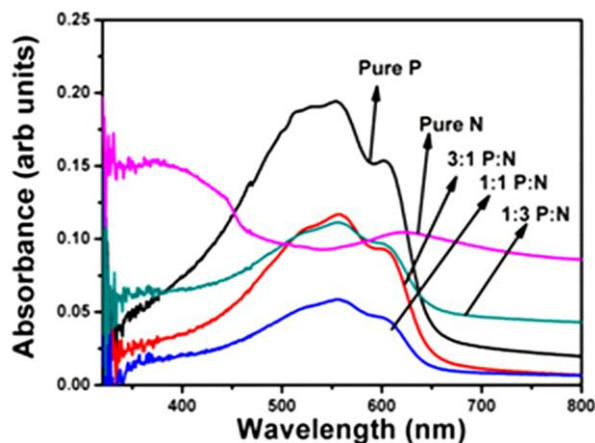
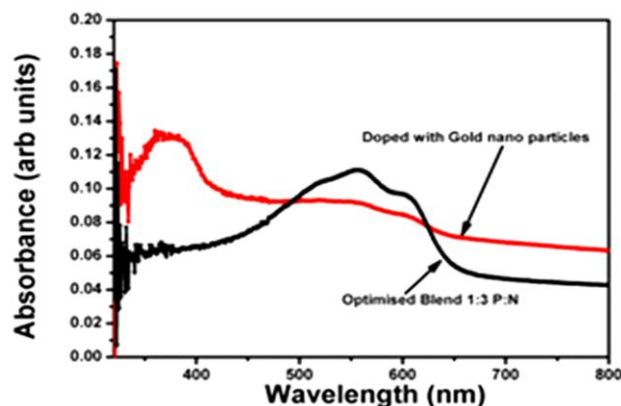Fig. 2. overlay presentation of absorbance spectra of polymer blends.

Fig. 3. Absorption spectra of 1:3 blend and gold nano particle doped 1:3 blend.

We have evaluated the band gap of these samples using Tauc's plot. The Tauc gap is often used to characterize practical optical properties of amorphous materials. The absorption coefficient of amorphous material is given by Tauc and Davis-Mott model

$$\alpha(v)hv = B\ (hv - E_{gap})^{m,}$$

where, E_{gap}, B, and hv are the optical gap, constant, and incident photon energy, respectively; $\alpha(v)$ is the absorption coefficient defined by the Beer-Lambert's law as $\alpha(v) = 2.303 \times A(\lambda)/d$, where d and A are the film thickness and film absorbance, respectively. In amorphous materials four types of transitions occur namely indirect forbidden transition, indirect allowed, direct forbidden and direct allowed transitions. These transitions are characterized by the m values 1/3, ½, 2/3 and 2 respectively [**6**, **7**].

Table 2. Results from Tauc's Plot.

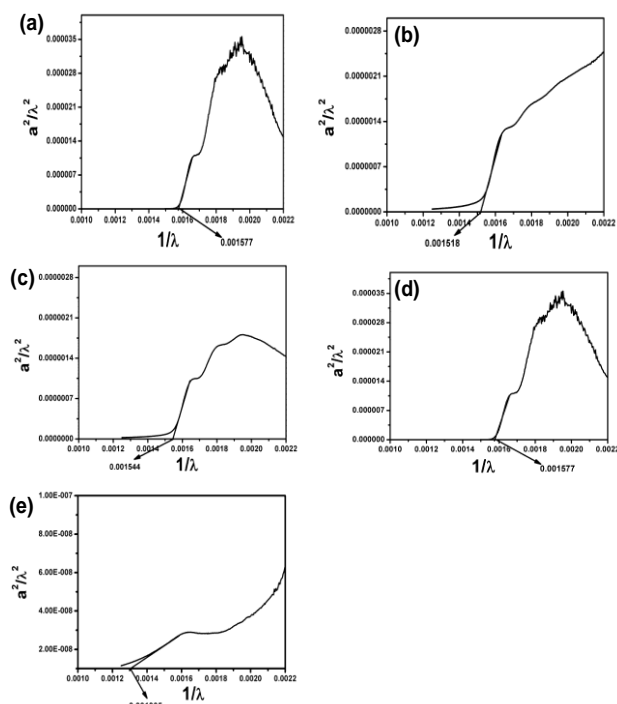| Sample	On set wavelength (nm)	Optical bandgap (eV)
Pure P	634.11	1.95
3:1 (P:N)	658.76	1.88
1:1 (P:N)	647.66	1.91
1:3 (P:N)	660.00	1.87
Pure N	766.00	1.61

Fig. 4. Tauc's plots of (a) Pure P, (b) 3:1 P:N   (c) 1:1 P:N   (d) 1:3 P:N   (e) Pure N.

For indirect allowed transition, m=1/2

$$\alpha(v)hv = B\ (hv - E_{gap})^{1/2}$$

The calculations from Tauc's plot shows that the onset wavelength of the optimized blend is 660nm which corresponds to a band gap of 1.9eV. The optimized blend is doped with gold nano particles of 10nm diameter, a stabilized suspension in citrate buffer using methyl alcohol as the dispersing agent. Nano doped blend is again spin coated and characterized by UV Visible absorption (**Fig. 3**). Absorption curve is extremely flattened with increased absorbance. The enhanced absorption is due to the Plasmon Resonance of gold particles in which the oscillating electric fields of a light interact with the free electrons causing a collective oscillation of electron charge that is in resonance with the frequency of visible light. These resonant oscillations are known as Surface Plasmon. For small gold nano particles, the Surface Plasmon Resonance phenomena causes an absorption of light in the long wavelength region of the visible spectrum. The construction of the solar cell using the Plasmon enhanced blend is the work under progress.

Conclusion

We have investigated UV- Visible absorption spectra for 3:1, 1:1, 1:3 blends of P3HT: NTCDA mixed p - n junction photoactive material along with their pristine glass coated films (Spin coating). Spectral analysis indicated that increased weight percentage of NTCDA in the blend has broadened the spectral region of absorption. 1:3 blend of P3HT: NTCDA shows a broad spectral response and selected as the best photo active blend. The

optimized blend has the least band gap of 1.87eV. By doping the optimized blend with gold nano dispersion, the absorption is further enhanced. The increased absorption is attributed to the Plasmon resonance. Even it is planned to carry out dye sensitization of the active blend. Finally we conclude that 1:3 blend of P3HT:NTCDA can be used as the best photoactive material for constructing a plastic solar cell and the construction of the solar cell is under progress.

Acknowledgements

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