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Analyzing p-type Conjugated Conducting Poly (diaminonaphthalene) Doped Poly (vinyl alcohol) Bulk Hetrojunction Film for Organic Solar Cells

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Abstract

Bulk Hetrojunction configuration for those electronics devices which require interpenetrating strength with large doner-acepter interfacial area is the matter of concern in microelectronics. At the same time developing p-type conjugated conducting polymers with easy synthesis, high charge carrier mobility, strong absorption properties and suitable energy gap for bulk hetrojunction (BHJ) are also required for sake of efficient applications. BHJ solar cell architecture, where in bulk, phase separation between the two components are required in controlled form are achieved by both accepter and donor materials which enhance the solar cell performance in terms of parameters like power conversion efficiency and fill factor. Poly (diaminonaphthalene) doped Poly (vinyl alcohol) (PDAN doped PVA),a p-type conjugated conducting polymer film, may be the materials for bulk semiconductor hetrostructure. The D.C conductivity at room temperature of PDAN doped PVA film was found to be 2.0408 x 10^{-4} mho m^{-1} which gives the mobility in the range of 0.43 cm^2/Vs. The economic chemical oxidation method was used for synthesizing PDAN doped PVA films. The Arrhenius plot provides the energy band gap of the order of 1.312 eV which is smaller than the limit 1.77 eV for approximately 700 nm range wavelength of solar spectrum for photovoltaic mechanism. The spatial parameter "redundance" calculated from Atomic Force Microscopy (AFM) which provides the fractal morphology of the sample, was found to be -0.18 for PDAN doped PVA film thus suggests for less disordered surface which satisfies the desired criteria for electronics applications.

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Keywords: Organic Solar Cell; Bulk hetro-junction; p-type conjugated polymer PDAN doped PVA film; Arrhenius plot; Redundance.

1. Introduction:

Harvesting the renewable solar energy by means of organic materials is one of the most important ways to obliged nature for sustainable environmental clean-up. Low cost, easy fabrication and biodegradability enhance the acceptability of electronic devices by using conjugated conducting polymer materials [1-3]. Organic solar cells (OSCs) fulfill the criteria when bulk hetrostructure [4-5] and blend film nano-morphology concepts are applied. If

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blending of donor and accepter materials occurs in a film, then large interfacial interpenetrating bulk hetrostructure network is achieved which enhances quantum efficiency of charge separation because the effective field so developed between two different polymer semiconductors causes dissociation of excitons into electron-hole pairs. Several donor-acceptor interfaces within Bulk-hetrojunction (BHJ) result in fast exciton diffusion and charge separation [6-7].

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Low band gap polymers as active material in solar cell mechanism follows a criterion that HOMO-LUMO energy gap should match the solar radiation for maximum absorption and for that those p-type conjugated polymers which have band gap energy less than 1.77 eV for mean solar radiation may be desired. Furthermore, for the bulk hetrojunction the selected materials are defined by work function which provides knowledge about electron and hole transportations between the band gap of HOMO-LUMO energy levels in bulk hetrojunction [8]. It is also important that the difference between energies between HOMO-HOMO donor/accepter and LUMO-LUMO donor/accepter levels of the two semiconductor levels is remains small therefore the mechanism of polymer solar cell will be satisfied. On the other hand, the 'responsivity' of the PSC depends on the movement of dissociated electrons and holes towards respective electrodes. Faster the movement and collection of charge carriers more the photon to electron conversion works.

Due to Peierls instability or distortion, the conjugated polymer shows unusual charge mechanism and the charge carriers are transferred by the nonlinear topological defects in the chain. Non-degenerate energy levels of conjugated polymers produce the optical properties [9] and therefore used in OSCs. Poly (diaminonaphthalene) (PDAN) is ideal p-type conjugated polymer with easily synthesis, low energy band gap and broad absorption band width, matched with charge mobility due to bulk hetro-structure and visible region spectra of sunlight. Non-degenerate ground-state levels causes the charge mechanism required for the optimum photo-conduction in OSC and PDAN doped PVA will provide one of the active material for the bulk hetrojunction.

Film morphology also affects the quantum efficiency of the OSCs. Roughness parameters, if result in many voids, creating resistance and decreases the charge mobility. Controlled growth bulk hetrostructure will prevent trapping of charges through disordered interpenetrating interfaces network. Roughness morphology of PDAN doped PVA film via Atomic Force Microscope (AFM) results highly desirable controlled structure for OSCs. When fullerene (C_{71}) derivative also doped inside the PVA film, the nano-structured voids generated on the surface of PDAN doped PVA film are filled by the fullerene derivatives forming a nano width channels between n-type and p-type organic material which is necessary condition for the diffusion length of excitons in organic electronic materials.

The concept of planer hetero-junction OSC was first experimentally introduced by Tang et al. with power conversion efficiency of around 1% [10]. The limitation of delay of charge carrier mobility towards their respective electrodes was rectified by introducing bulk hetero-junction which involves multiple channels for charge carriers, introduced by Hiramoto et al. [11].The realization of BHJ contained OSC was first published by the team of Heeger and coworkers in 2005 [12]. From the last decade, so many research efforts are pronouncing to proclaim the performance in the means of power conversion efficiency values more than 10% for PSCs [13-17].

In the present work taking an account of high efficiency of OSCs, ideal p-type conjugated polymer PDAN doped PVA films are characterized via several parameters by analysis of conducting properties through charge mobility and band gap energy and morphological properties. Also, polymeric organic solar cells with known ideal n-type organic material for example, fullerene derivatives, have been modeled while p-type organic material i.e. PDAN which are doped inside the PVA, has been experimentally investigated and presented in this paper. The film satisfies required mechanical properties with electrode graphene sheet and its derivatives which show both anode and cathode ends [18-19]. Graphene sheet becomes transparent and the sunlight is easily transmitted through the graphene electrode and then incident on active region i.e. bulk hetrostructure network which will increases the collection of charges responsible for photocurrent [20]. Authors believe that the durability, mechanical, electrical, structural, and optical properties will satisfy the criteria required for designing OSCs.

2. Methodology:

PVA (99% hydrolyzed, MW 85,000 Da) was purchased from Hi Media Chemicals, Mumbai, India. The

monomer DAN was purchased from Merck Chemicals, Mumbai, India. All other reagents used in the study were of high purity grade.

The method adopted for synthesizing PDAN doped PVA film is chemical oxidation. In a typical experiment, 5 g PVA was dissolved in 100 mL of hot distilled water and to this solution pre-calculated amount of glutaraldehyde was added as cross-linking agent. Now, the whole mixture was kept in a Petri dish (Corning glass, 2.5" diameter) in hot air oven at 50°C for 48 h. After heating up to required time, the whole mass converted into semi transparent film. The dry film was equilibrated in distilled water for a week to leach out unreacted chemicals. The swollen gel was than dried at room temperature, cut into rectangular size piece and stored in air tight plastic bags [21].

2.1. Proposed Experimental Model:

Required quantity of DAN and Buckminsterfullerene C_{71} derivative will be dissolved in common solvent acetonitrile and then the PVA gel so prepared will be allowed to soak in the DAN and Buckminsterfullerene solutions for 24 h. The DAN containing swollen gels will be dried and dipped into oxidizing agent, ammonium-per-sulphate. As the polymerization proceeds, the semi transparent gels turn into black and when seen in white light its color looks dark.

Graphene sheet with few-layered will produce by low-temperature exfoliation and reduction of graphene oxide in ambient atmosphere on the substrate which will be PDAN and C_{71} derivative doped PVA, laying out on both sides [22].

2.2. Experimental:

The DC conductivity was measured with four probe technique including Keithley 6221 DC and AC sources and Keithley 2182A nano-voltmeter. The DC conductivity measurements were performed at temperature from 260C to 550C under ambient conditions. The thickness of the film was measured to be 0.30 mm and the distance between two probes was 2 mm. All these measurements were carried out in Advanced Centre for Materials Science (ACMS) lab, Indian Institute of Technology, Kanpur, INDIA. The AFM analysis was carried out from the instrument NTEGRA Prima, manufactured by NT-MDT at Centre of Nano-science and Nanotechnology, Sathyabama University, Chennai, INDIA. NTEGRA Prima has a built-in optical system with 1 μm resolution, which allows imaging the scanning process in real-time. The FESEM was measured from instrument FESEM-SUPRA 55 - CARL ZEISS, GERMANY at Centre of Nano-science and Nanotechnology, Sathyabama University, Chennai, INDIA.

3. Results and Discussion:

There are some issues related to the low efficiency of the BHJ containing OSCs. Due to different chemical and physical nature of the multiple polymers and the large differences in the HOMO-LUMO molecular band gaps of the mixture of the polymers, the parameters which improve the working of solar cells may get suppressed [23]. However availability of high performance bulk hetro-junction contains donor polymers e.g. PDAN doped PVA films may increase the quantum efficiency of the OSC. It is due to weak inter and intra molecular interactions (van der Waals forces) between the PDAN doped PVA domains that enables the exciton dissociation. The presence of dielectric polymer (PVA) increases the mobility of electron-hole pair form the nano-channels to their respective electrodes. **Figure 1** shows the model of possible high efficiency of the BHJ contain OSC. In this paper authors reported only the possible character of p-type conducting polymer (because the physical and chemical characterization of Fullerene in the application of solar cell were elaborated in the many reported papers) for BHJ based OSC [24-25].

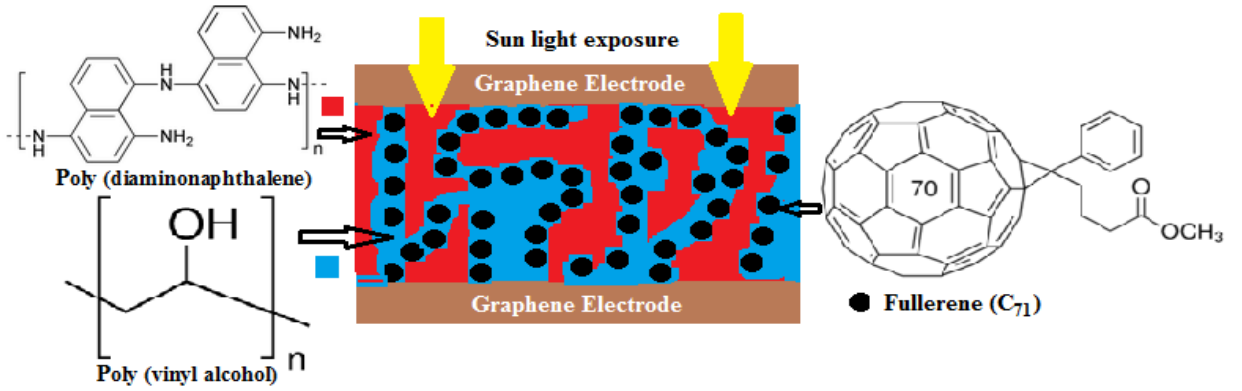


Fig. 1: Modeling of bulk hetro-junction Organic solar cells

Figure 2 demonstrates the electrical characterization of PDAN doped PVA film. **Figure 2(a)** shows the graph between log of current and log of voltage at temperature range from room temperature to 55^0C for PDAN doped PVA films. The abrupt change in voltage with increase in temperature shows the semiconductor nature of the PDAN doped PVA film. The conductivity of the sample is determine by using the four probe method in which the value of (W/S) is equal to 0.15 and the value of G_7 becomes 9.5, is 2.041 x 10^{-5} Scm^{-1}. The charge carrier mobility is measure by Hall experiment and it is found in the range of 0.43 cm^2/Vs. **Figure 2(b)** shows the temperature dependence of resistivity plots at different constant current for PDAN doped PVA films. By finding the slop of the graph the band gap energy for the film is in the range of 1.30 eV to 1.70 eV. The optimally performing wavelength of monochromatic light for solar cell is calculate by the formula,

$$\lambda_{opt} \sim [1240/E_g\,(eV)]\ nm \qquad (1)$$

and by putting the experimentally obtain value of E_g in Equation 1 , the λ_{opt} is found in the range of 700 nm to 950 nm which is suitable for photovoltaic mechanism for the incident solar spectrum.

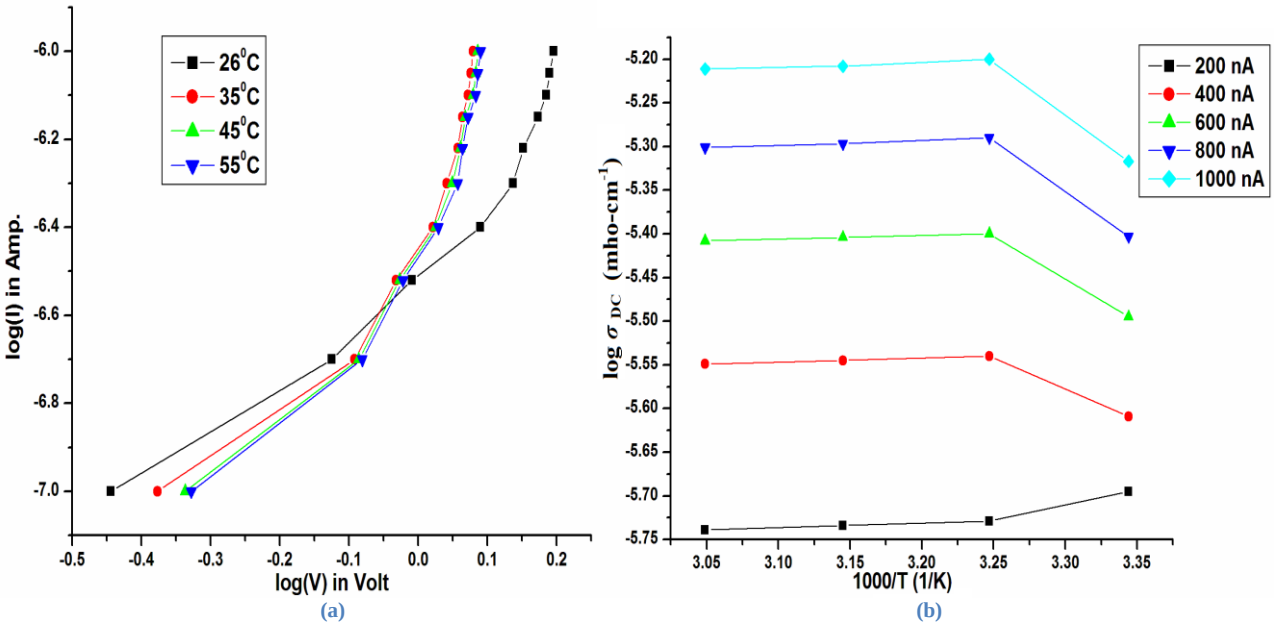


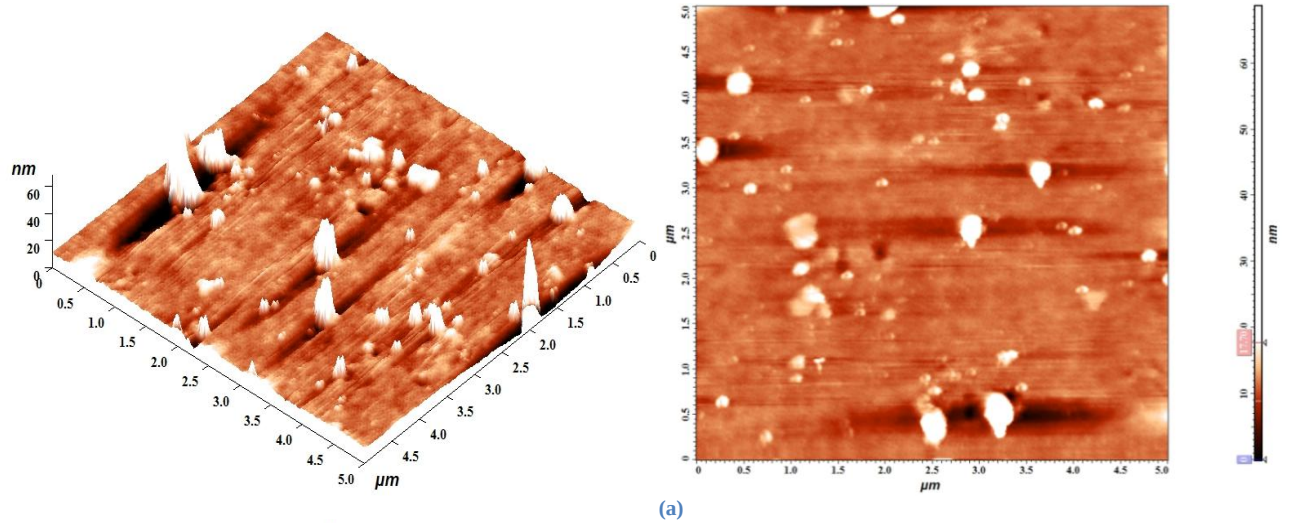
Fig. 2: Electrical characterization (a) electrical conductivity (b) temperature dependence resistivity plots of poly (diaminonaphthalene) doped poly (vinyl alcohol) film

The spatial parameters e.g. Redundance and Entropy measure the richness of experimental samples morphology connecting with the degree of order or disorder in the grain structure distribution [26]. Lower the values of the redundance, least disorder of the morphology of the films are obtained. The comparative values of spatial parameters for PVA, monomer doped PVA and PDAN doped PVA films are shown in **Table 1**.

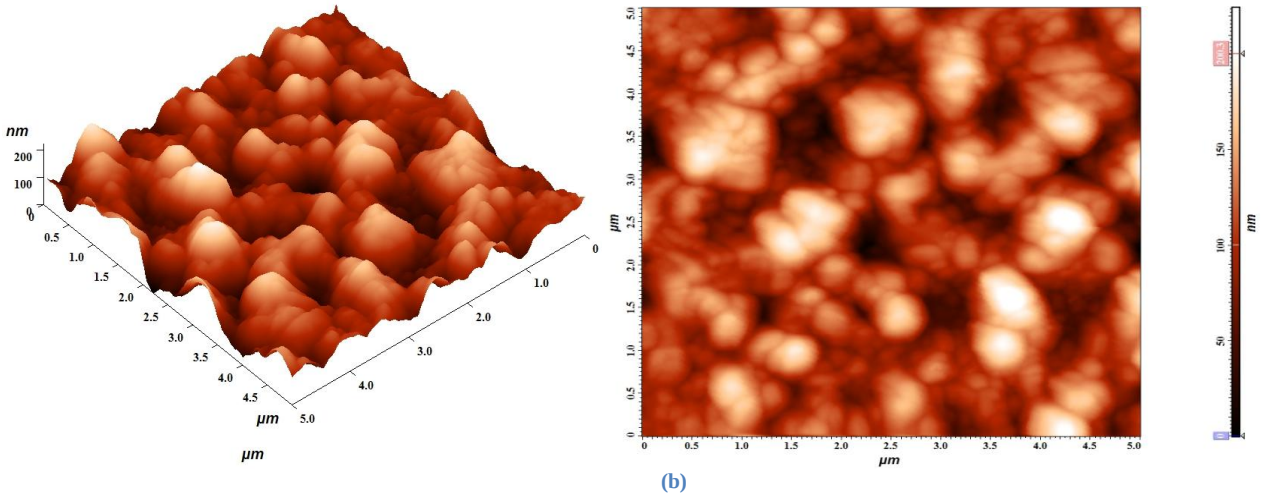
Figure 3 (a), (b) and (c) shows the surface morphology of the experimental films and the least disorder is shown for PDAN doped PVA film which will be better for layering graphene sheet on BHJ contain PDAN doped PVA films.

Table 1: Comparison of different samples with spatial parameters

Parameter	PVA film	DAN doped PVA film	PDAN doped PVA film with acetonitrile solvent
Scanning area	**10 X 10µm^2**	**10 X 10µm^2**	**10 X 10µm^2**
Entropy	6.79	11.05	12.63
Redundance	0.085	-0.23	-0.18



(a)



(b)

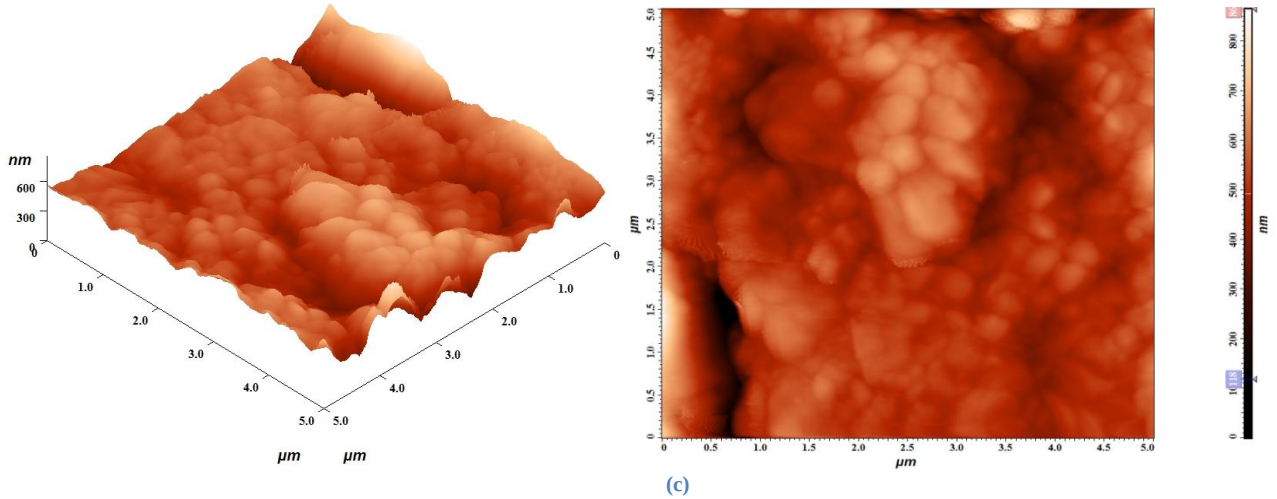


Fig. 3: 2D and 3D images of the (i) PVA film (ii) DAN doped PVA film (iii) PDAN doped PVA film with acetonitrile solvent

Figure 4 (a) and (b) demonstrate the Field Emission Scanning Electron Microscope (FESEM) images of PVA and PDAN doped PVA films. **Figure 4 (b)** clearly shows the gaps (nano structured channels) between PDAN domains which are fulfilling the criteria of bulk hetro-junctions. The sizes of the PDAN domains are in the range of 300 nm to 400 nm which results the spectral conversion of sunlight into power and enhances the solar cell parameters.

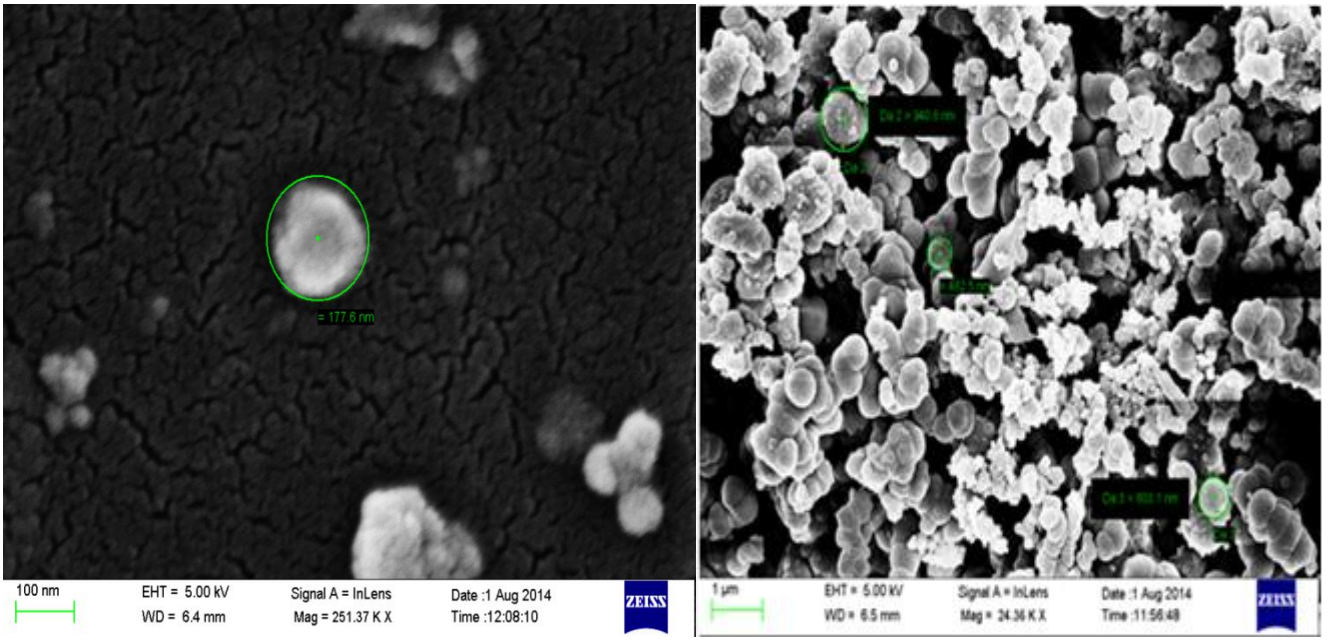


Fig. 4: FESEM images of (a) PVA film and (b) PDAN doped PVA film

4. Conclusions:

The current-voltage graph reveals that the PDAN doped PVA films behave as semiconductor and the conductivity is found to be 2.041 x 10^{-5} Scm^{-1}. As the temperature increases the conductivity of the films also increases and found to be six fold greater than native PDAN materials. The energy band gaps obtained is suitable for

solar spectrum and hence for BHJ contains OSCs. The AFM analysis and different spatial parameters extracted there from suggested that the PDAN doped PVA films are smooth at the sub-nanometer scale.

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