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Enhancement of efficiency of Phenosafranin based organic photovoltaic devices using nano particles

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Abstract: In this work the effect of incorporation of TiO_2 and ZnO nano particles on Phenosafranin dye (PSF) based organic photovoltaic devices has been investigated. The photovoltaic effect for the cell prepared with PSF solution is quite poor. The current density (J_{sc}) obtained for this cell is 0.0389 $\mu A/cm^2$. For the cells prepared with PSF solution mixed with TiO_2 and ZnO nano particles J_{sc} becomes 3.340 and 0.665 $\mu A/cm^2$ respectively. Nano particles play important roles in different ways. It acts as charge acceptor which assists the charge separation process. In addition to that it may reduce the series resistance of the cell which enhances the efficiency. The confinement of light energy due to multiple reflections by the nano particles has been also discussed. Due to the presence of these nano particles the incident light is scattered and the interaction time with the optical energy with the dye is enhanced causing the higher absorption of photon.

Keywords: PSF; TiO_2 nano powder; ZnO nano powder; Diffused scattering of light energy

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1. Introduction

It is well known that though the performance of organic photovoltaics has been developing steadily, these devices still faces fundamental limitations in efficiency and stability that needs to be overcome to make them competitive with inorganic solar cells. The remedies that are being used widely by scientists are to develop new device structures, introduction of new dyes, changing of different process techniques, incorporation of nano particles, etc. Recently there are several reports on the advances of different properties and applications of various nano materials [1–10]. Absorption of photon, generation of charge carriers due to the absorption and the separation of the charge carriers towards the respective electrodes are essential criteria of any organic photovoltaic devices. The efficiency will be enhanced as fast as the charges are being collected by the electrodes. For faster charge separation process a larger interfacial area is required for the dissociation of the generated electron hole pairs. The extra interfacial area may be provided by the incorporation of different nano particles. Nano scale metal structures embedded in organic devices could also potentially be beneficial in improving the light absorption, as well as the charge separation and charge collection processes [11–14]. In general, nano particles act as a coupling device to scatter incident light both in the forward direction and laterally into thin film [15–17]. The light energy is scattered by the nano particles and stays for more time within the active medium and hence more number of photons can be absorbed in the dye medium. These nano particles can produce photoexcited holes or radicals due to the adsorption of light with energy greater than their band gap. In the nano particle based organic photovoltaic devices carriers need to diffuse a substantial distance so that it can be extracted by the electrodes [18]. Due to the large interfacial area of these nano particles faster charge separation process occurs helping to increase the power conversion efficiency of the device. However, the exact role of the nano particle is not clear. It is expected that the nano particle plays a dominant role to control both the optical and electrical properties. The dependence of size and concentration of these nano particles on the performance of the devices need to be investigated.

In our work the effect of incorporation of different nano particles in Phenosafranin (PSF) based organic photovoltaic device has been studied. PSF is one of the most

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important cationic dyes of the phenazinium group of compounds. The cell prepared with PSF has been characterized. To see the effect of nano particle two different nano particles namely TiO$_2$ and ZnO are incorporated to the PSF cell. These two cells termed as TiO$_2$ cell and ZnO cell. These cells are characterized and the result has been compared and discussed.

2. Experimental details

Structure of PSF (3,7-diamino-5-phenylphenazinium chloride) is shown in Fig. 1(a). As mentioned earlier it is one of the most important cationic dyes of the phenazinium group of compounds. It has planar conjugated rigid structure. Phenazinium dyes (Sigma-Aldrich, Germany) have extensive applications in semiconductors, as energy sensitizers, in probing micro heterogeneous environments, and in many biological applications in photochemistry [19]. The structures of the TiO$_2$ and ZnO nano particles (Sigma-Aldrich, Germany) are shown in Fig. 1(b), (c) respectively. To prepare the cell, Indium Tin Oxide (ITO) coated glass was used as the front electrode while Aluminium coated on mylar sheet abbreviated as Al–M was used as the back electrode. In our early work [20] it was reported that

performance of Al–M sheet as back electrode is better than ordinary Al sheet since in the former case the reflectivity is quite high which enhances the optical energy confinement within the film to multiply the light absorption by the organic dye. Poly vinyl alcohol (PVA) which is highly viscous in nature is used in this work to stick the dye solution on the glass plate.

To prepare the PSF solution 30 ml distilled water was taken in a cleaned beaker in which 5 g of PVA was added and stirred with a magnetic stirrer for 30 min at 80 °C to get a clear solution of PVA. In this PVA solution 2 mg of PSF dye was added and again stirred well for 10 min. This solution was divided in three parts in three pre-cleaned test tubes. One test tube was kept aside. In other two test tubes 2 mg of TiO$_2$ and 2 mg of ZnO nano particles were mixed separately to prepare PSF solution with TiO$_2$ nano particles and PSF solution with ZnO nano particles. On a pre-cleaned ITO coated glass the prepared PSF solution was spin coated at a speed of 1,500 rpm and after that the film was dried at a speed of 3,500 rpm. Similarly on an Al–M sheet the same solution was spin coated. Both these electrodes were sandwiched together to form the PSF cell. The cell was kept in vacuum for 12 h to dry. In a similar manner PSF solution mixed with TiO$_2$ and ZnO nano particles were spin coated to prepare the TiO$_2$ and ZnO
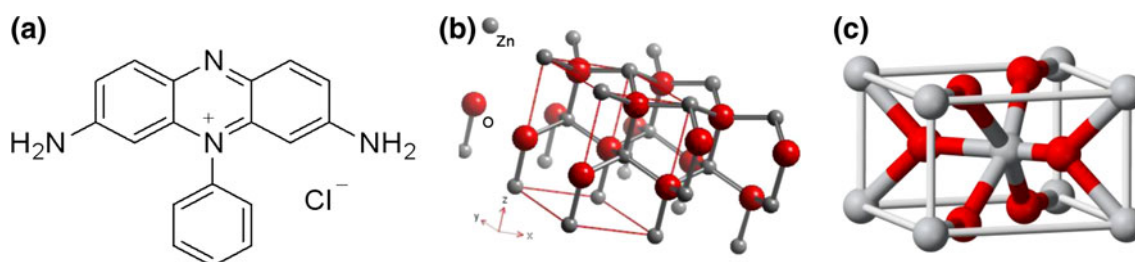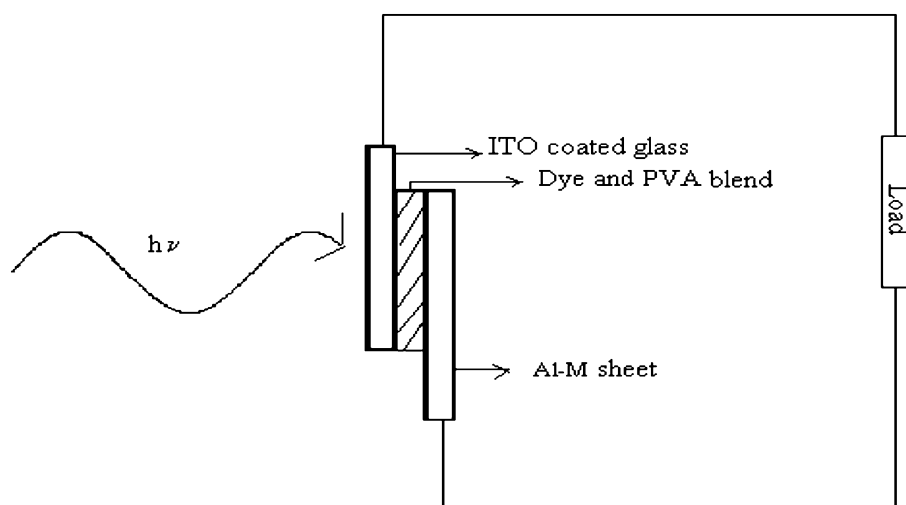

Fig. 1 Structure of (**a**) PSF dye, (**b**) ZnO nano particle and (**c**) TiO$_2$ nano particles

Fig. 2 Schematic diagram of the cell and also the experimental set up for photovoltaic measurements
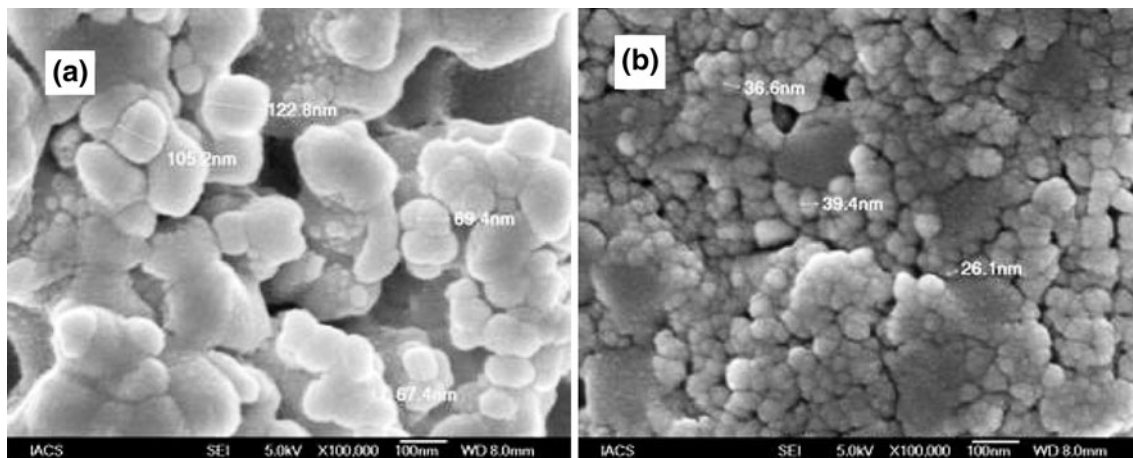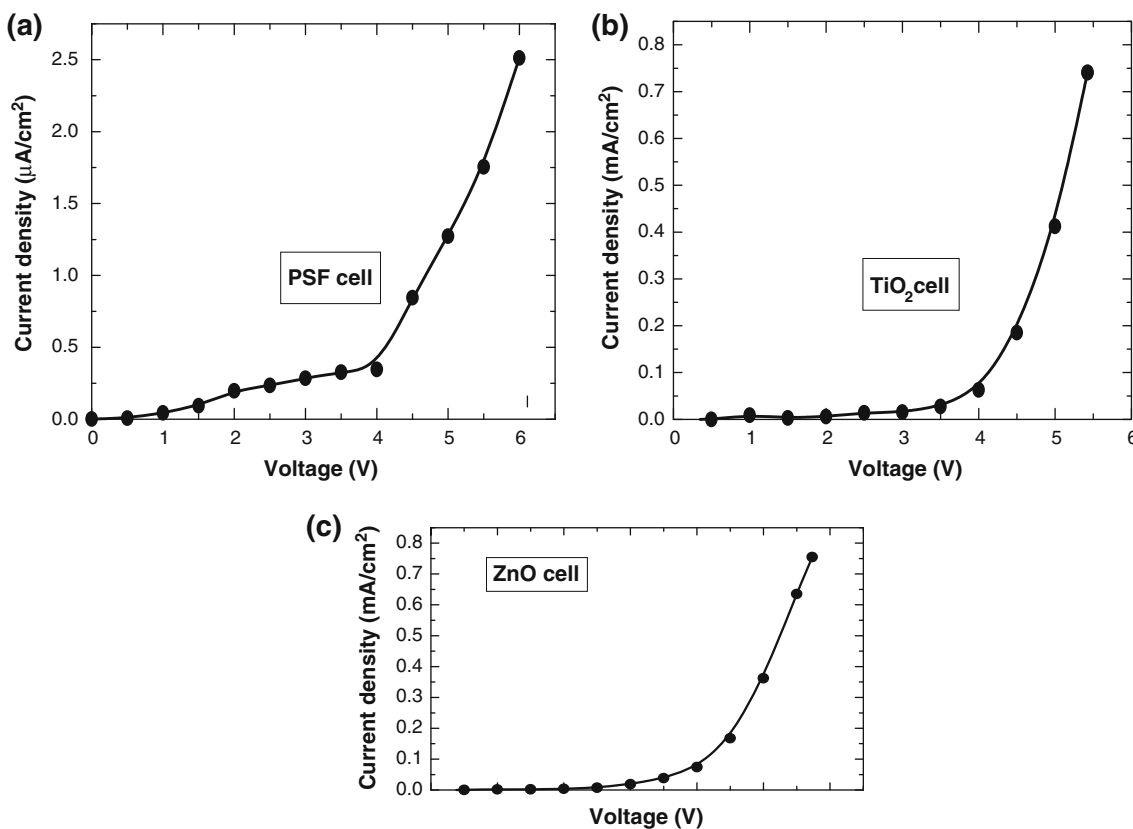
Fig. 3 SEM images of (**a**) TiO$_2$ cell and (**b**) ZnO cell

Fig. 4 Dark I–V curves for (**a**) PSF cell, (**b**) TiO$_2$ cell, and (**c**) ZnO cell

cells. The prepared cells were kept in vacuum for 12 h. These cells were characterized after proper drying.

Scanning electron microscopy (SEM) images were taken for both TiO$_2$ and ZnO cells in a JEOL field emission scanning electron microscope (JSM-6700F) operating at an accelerating voltage of 5 kV. The dark current–voltage (I–V) was measured with Keithley 2400 source measure unit. The bias voltage was varied from 0 to 6 volts in 0.5 V steps

with 500 ms delay. The photovoltaic measurement was also performed with a solar simulator (Model 150 W Newport Corporation). The current was measured with a digital current nanometer and voltage was measured with Keithley 2000 multimeter. Figure 2 shows the schematic diagram of the experimental set up for the photovoltaic measurements. The experiment was performed in the open atmosphere of the laboratory at nearly 23 °C.

3. Results and discussion

Figure 3(a), (b) show the SEM images of the TiO_2 cell and the ZnO cell. It is observed that there is a tendency of coagulation of the nano particles. Due to the presence of PVA the nano particles get coagulated. The concentration of the PVA, which restricts the movement of charges, should be used as minimum as possible.

The dark I–V characteristics are shown in Fig. 4(a)–(c) for PSF cell, TiO_2 cell and the ZnO cell respectively.

From these figures it is observed that the current is quite less for the PSF cell and it increases for the TiO_2 and ZnO cell. A change of threshold voltage is also observed. To get insight about the conduction mechanism these data have been analysed considering the effect of traps in these systems.

Evaluation of the electrical performance for the photovoltaic cells can be done by measuring dark I–V. It has been reported that dark I–V measurement helps to determine the series resistance of cells [21]. Dark I–V measurements are commonly used to analyze the electrical characteristics of solar cells, providing an effective way to determine fundamental performance parameters.

In our early work [22] we have reported that in organic materials trap charges play a dominant role in the current conduction process. These traps introduce energy levels inside the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the organic layers [23]. Due to the trap levels, a major part of the carriers injected from the electrodes are trapped and are generally crowded near the electrodes. When this process is dominant, it is called trap charge limited conduction process. This is a special case of the general space charge limited (SCL) regime. The process is referred to as trap-free SCL conduction when the space charges are dominantly free carriers. The distribution of trap energy level is generally described by one of the following ways: (i) an exponential distribution, (ii) discrete levels, and (iii) a Gaussian distribution. Assuming an exponential energy distribution, trap charge concentration (n_t) may be expressed as

$$n_t = H_n \exp\left(\frac{F_n}{kT_c}\right) \tag{1}$$

where H_n is the trap density, F_n is the electron Fermi energy, κ is Boltzmann constant, and T_c is characteristic
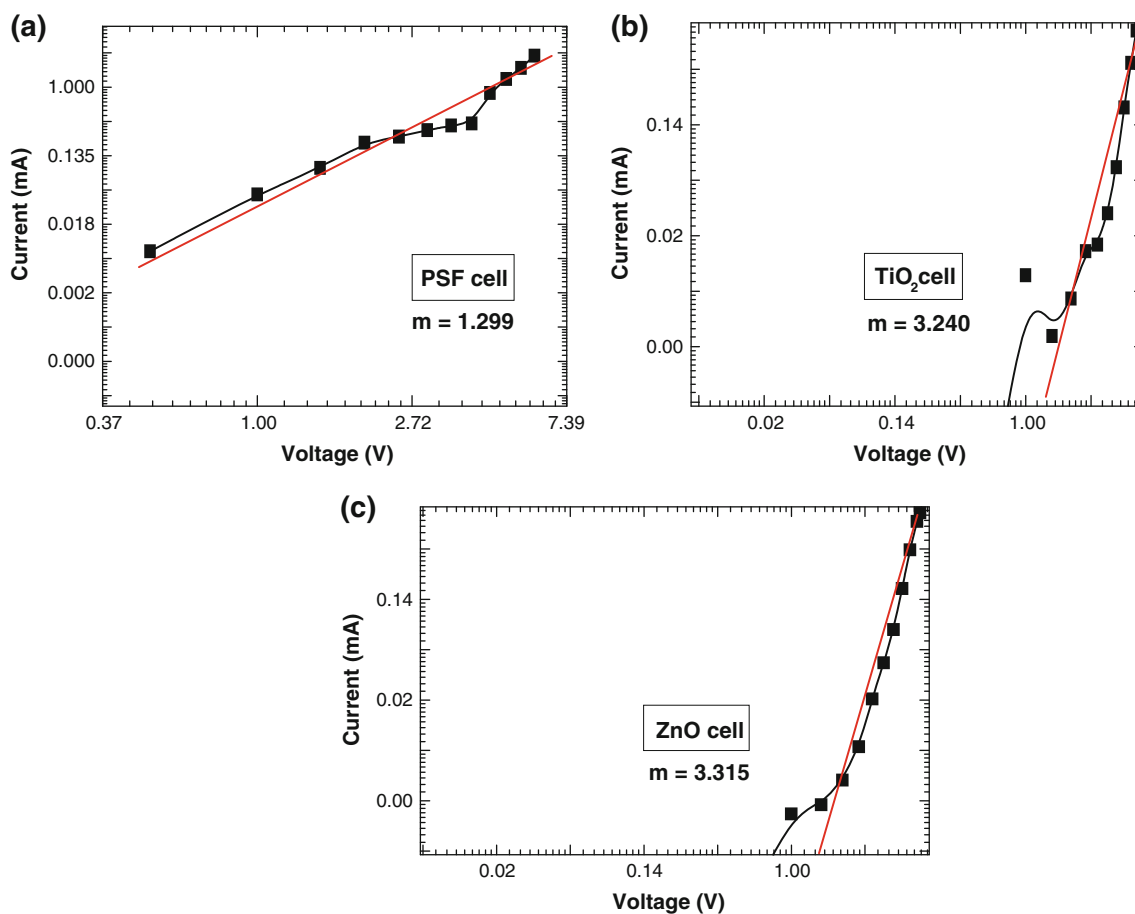

Fig. 5 ln I–ln V curves for (a) PSF cell, (b) TiO_2 cell, and (c) ZnO cell

temperature of the exponential trap distribution (i.e., $T_c = E_c/\kappa$, where E_c is the characteristic trap energy). Solving the Poisson equation with this form of trap distribution, the I–V characteristic is calculated and written in the following form [23]

$$J = N_c \mu q^{1-m} \left(\frac{m\varepsilon}{H_n(m+1)} \right)^m \left(\frac{2m+1}{m+1} \right)^{m+1} \frac{V^{m+1}}{L^{2m+1}} \quad (2)$$

where N_c is the effective density of states in LUMO or HOMO, μ is the mobility of majority carrier, L is the thickness of the layer, ε is equal to $\varepsilon_0 \varepsilon_r$ with ε_0 being the permittivity of vacuum and ε_r the dielectric constant, V is the applied voltage and $m = T_c/T$, T_c is a "characteristic temperature" that describes the trap distribution. The most notable feature in the above equation is the power law dependence of [23]

$$J \sim V^{m+1} \quad (3)$$

assuming that the thickness of the cell is constant. In this case also the dark I–V curves are analysed to find the characteristic temperature.

Table 1 Extraction of 'm' values from ln I–ln V curves

Cell composition	Value of 'm'
PSF cell	1.299
TiO$_2$ cell	3.240
ZnO cell	3.315

Using Eq. 3 the values of m are calculated from ln I–ln V curves shown in Fig. 5(a)–(c) and are listed in Table 1.

Figure 6(a)–(c) show the the current density–voltage (J–V) diagram in fourth quadrant of three cells under an illumination of 100 mW/cm^2 from a solar simulator. The parameters of interest like open circuit voltage (V_{oc}), short circuit current (I_{sc}), Fill Factor (FF) and power conversion efficiency ($\eta\%$) are calculated from these curves and are listed in Table 2. It is evident that the Jsc obtained for the PSF cell is quite poor compared to that for the TiO$_2$ cell and ZnO cell. The FF obtained for this cell is also much lower than that of the other two cells. This may be due to the reason that series resistance of the cell is very high.
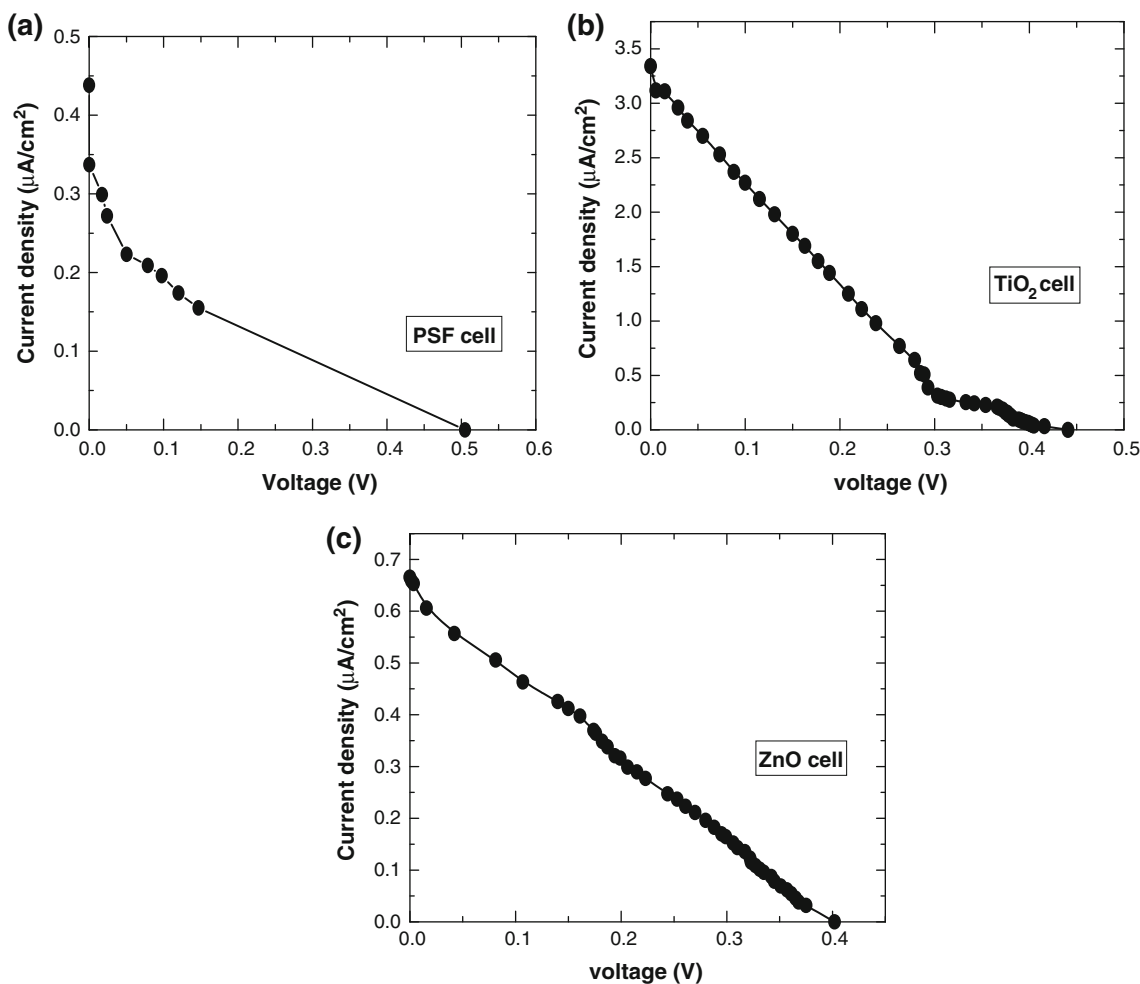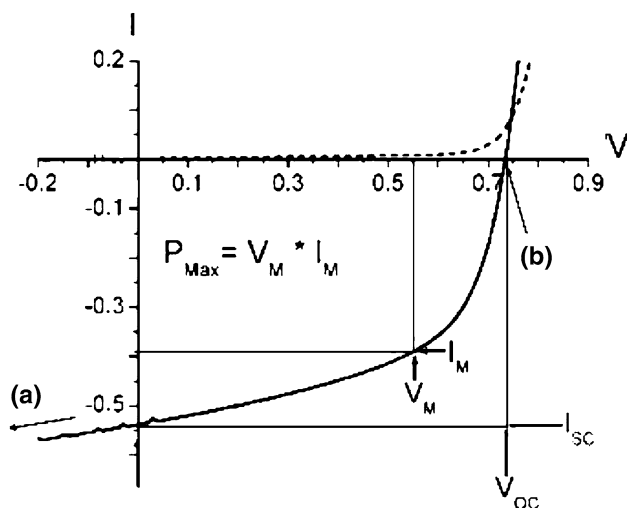

Fig. 6 Photovoltaic measurement for (**a**) PSF cell, (**b**) TiO$_2$ cell, and (**c**) ZnO cell

Table 2 Extraction of different photovoltaic parameters

Cell composition	V_{oc} (mV)	Jsc (μA/cm^2)	FF	Efficiency %
PSF cell	505	0.0389	0.10	0.0196×10^{-4}
TiO$_2$ cell	441	3.340	0.19	2.798×10^{-4}
ZnO cell	402	0.665	0.24	0.6422×10^{-4}

Fig. 7 Light I–V curve of an organic photovoltaic device (*dotted line* dark, *solid line* illuminated). V_{oc}, I_{sc}, V_m and I_m are shown in the figure

The reduction of FF can also arise from the chemical degradation of the metal–polymer interface [24]. When the nano particles are incorporated the series resistance decreases which in turn increases the FF.

The typical characteristic of a solar cell is shown in Fig. 7. The maximum generated photocurrent under short-circuit conditions is shown by the point (a) and the photogenerated current is balanced to zero shown by the point (b). At a certain point, denoted as maximum power point, the product between current and voltage the power

output is the largest. To determine the efficiency of a solar cell, this power needs to be compared with the incident light intensity. Generally, the FF is calculated as
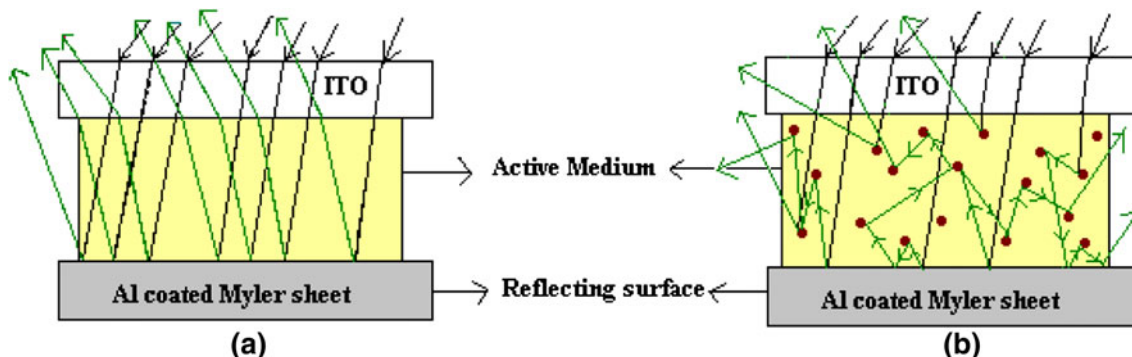
$$FF = \frac{I_m \times V_m}{I_{sc} \times V_{oc}} \tag{4}$$

The power conversion efficiency (η) can be written as

$$\eta\% = \frac{P_{out}}{P_{in}} = \frac{FF \times I_{sc} \times V_{oc}}{P_{in}} \tag{5}$$

Table 2 shows that the incorporation of the nano particles enhances Jsc as well as η of the cells. This increase in Jsc and hence in η are nearly 85 and 143 times respectively higher for TiO$_2$ cell and 20 and 33 times higher for ZnO cell than PSF cell. It is also interesting to note that for both the TiO$_2$ and ZnO cell Jsc increases but for TiO$_2$ cell Jsc is much higher than that of ZnO cell. Though it is difficult to compare the enhancement in efficiency for two different particles still in literature [25] it was found that faster charge separation process occurs in the TiO$_2$ than in ZnO. It was also observed that the charge separation process is extremely fast for the organic dyes absorbed on the surface of TiO$_2$ rather than the organic dyes absorbed on ZnO. The charges are separate within 50 fs in TiO$_2$ whereas it takes around 10 ps for ZnO cell [25] which indicates that the charge separation rate is nearly 200 times faster in TiO$_2$ in comparison to ZnO. This difference is quite significant in the nano domain which may be a reason for such a wide difference in current density.

The increase in current density may be explained on the basis of two facts. It may be attributed to optical and electrical property of the nano particles. The optical phenomenon that is happening within the cell may be understood from the schematic diagram given in Fig. 8. In the Fig. 8(a) it is shown that light falls on the surface of the cell without any nano particle. When light beam is incident on this cell a part of it gets reflected back from the outer surface of the cell and most of the part gets transmitted into

Fig. 8 Schematic diagram to show the confinement of light energy of the cell (**a**) without any nano particle and (**b**) with nano particles and *filled circle* indicates the nano particles in the active medium

the cell. This transmitted light rays get reflected back from the upper surface of the back electrode and its get back in the outer medium. The percentage of absorbed light is quite small.

To understand the multiple reflections by nano particles schematic diagram of the cell is shown in Fig. 8(b). The diagram shows that the incident light, which enters into the cell, is scattered by the nano particles repetitively within the cell and confined in the cell for a longer time. This ensures that the light absorbed in the active medium is higher than that of the cell without nano particles.

The large interfacial area of the nano particles also assists in accepting the dissociated charges and helps to reach them towards respective electrodes. As mentioned before it also decreases the series resistance of the cell which in turn increases the current density of the devices. Further work is needed to concretize this idea. It is also reported [26] that in donor–acceptor interface of an organic heterojunction, nano particles may enhance photon absorption by concentrating the energy of incident radiation close to the junction.

4. Conclusions

In this work an attempt has been made to highlight the role of the nano particles in the Phenosafranin dye based organic photovoltaic device. It is observed that nano particles enhance power conversion efficiency of the organic devices. The cell without nano particle shows lower efficiency than the cells with nano particles. This is due to the fact that nano particles provide a large interfacial area which assists the charge separation process. The nano particles also act as the scattering centre of the incident radiation. The diffused scattering by the nano particles confines more light energy for a longer time in the active medium causing more absorption of photons by the medium which is basically responsible for showing higher efficiency of the device. It is also observed that the device efficiency is high in TiO_2 cell than that of the ZnO cell since the charge separation process in TiO_2 is quite faster in comparison to ZnO.

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