



Conference Paper

Charge Carriers Motion in P3HT:CappedZnO Nanoparticles Blend Films; Impact of Capping Agents

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Abstract Blend of conjugated polymer poly(3-hexylthiophene) or P3HT and Zinc Oxide nanoparticles (ZnO-NP) has been intensively used as active material for high performance hybrid solar cells. However, agglomeration of ZnO-NP hinders efficient charge carriers transfer both from P3HT to ZnO-NP and their transport within ZnO-NP which cause to low performance of solar cells. Capping of ZnO-NP is currently applied to avoid this agglomeration effect. In this study, we used three different capping agents to cap ZnO-NP, namely small semiconducting molecules squaraine, 2-naphthalene and insulating polymer polyvinylpyrrolidone. We conducted temperature dependence of photoinduced infrared absorption spectroscopy to study charge carriers motion in the P3HT:cappedZnO nanoparticles blend films. The measurement was carried out with light irradiation of 532 nm and temperature ranging from 78 to 300 K. The spectra were analyzed by a bimolecular carrier recombination method with Arrhenius activation energy. Two parallel charge carrier recombination processes are observed, namely polarons recombination along polymer chain (intra-chain) and inter-chain polarons recombination in the P3HT-chains. At low temperatures, polarons recombine along polymer chains (intra-chain) with activation energy between 19-23 eV for all samples. However, the inter-chain polaron motion is influenced by capping agents as shown by a variation in its activation energy ranging from 28 to 58 eV.

Keywords: Hybrid solar cells, ZnO nanoparticles, Capping Agents, Charge Carriers Motion

1. Introduction

Hybrid conjugated polymers inorganic nanocrystals solar cells have been intensively studied in the past decades due to their potential for low-cost and high performance renewable energy devices. The combination of flexibility and relative easy to control the optoelectronic properties of conjugated polymers and metal oxide nanocrystals, high performance of hybrid solar cells is expected to be realized. Although, many attempts have been carried out, the power conversion efficiency (PCE) of hybrid solar cells is still in the range of 3-4% [1-2], which is far below the PCE of fully organic solar

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cells which has already reached 11% [3]. Three main issues are identified as the cause of low PCE of hybrid solar cells, i.e. the agglomeration of nanocrystals, the difficulty to control the morphology of the blend conjugated polymers-inorganic nanocrystals and the lack of understanding of charge carrier motion in the active layer of hybrid solar cells.

Conjugated polymer poly(3-hexylthiophene) or P3HT has been frequently used as a model material for donor material of polymer and hybrid solar cells due to its superior optoelectronic properties such as high absorption coefficient, high hole mobility and easy to be formed in thin films by use of low cost and simple methods. Meanwhile, metal oxide nanoparticles, in particular zinc oxide nanoparticles (ZnO-NP) has been widely developed as donor material for hybrid solar cells due to its superior optoelectronic properties and its relatively easy to be synthesized by using solution methods. However, the agglomeration of ZnO-NP causes ineffective charge transfer of exciton from P3HT and electron transport within ZnO-NP and to the electrode leads to the low PCE of hybrid P3HT:ZnO-NP solar cell. ZnO-NP is therefore must be capped to avoid the agglomeration. Small molecules are commonly used as capping agents to avoid the agglomeration of metal oxides nanoparticles [4,5].

In this paper, we report our study on charge carriers motion in active layer of hybrid solar cell based on blend of P3HT:ZnO-NP uncapped and capped with three different materials. We used small semiconducting molecules squaraine (SQ) and 2-naphthalene (2-NT) and insulating polymers polyvinylpyrrolidone (PVP) as capping agents to avoid agglomeration of ZnO nanoparticles. Photoinduced infrared absorption (PIA) spectroscopy is used to study charge carrier motion in the blend films of P3HT:capped ZnO-NP. PIA enables us to observe the positive charge carrier or positive polaron motion in the film to clarify the charge recombination process that affect the PCE of solar cells [6]. In this study, we report temperature dependence of PIA spectra of blend P3HT:capped ZnO-NP films to obtain the activation energies of the recombination process of positive and negative carriers in the films and to clarify the effect of capping agents on the charge carrier transport in the hybrid P3HT:ZnO-NP films.

2. Experimental Method

ZnO-NP was synthesized by use of sol gel method as described in our previous work [7]. The ZnO-NP and PVP are dissolved in methanol, whereas the P3HT, SQ, 2-NT were dissolved in chlorobenzene (CB). The optical absorption of each solution and their blend were measured by use of T70+UV-Vis spectrometer. The particle size of ZnO-NP is measured by Transmission Electron Microscopy (TEM JEOL JEM 1400). Blend thin films of P3HT:capped ZnO-NP were prepared by use of spin coating technique on BaF₂ substrates. For each sample, 33 mg of P3HT was dissolved in 1 ml CB and 15 mg of ZnO-NP were dissolved in 1 ml mixed solvents containing 95% CB and 5% methanol. Both solutions were ultrasonicated for 15 minutes. Small amount of capping agent solution was added to the ZnO solution prior to ultrasonication process. After both solutions were well mixed forming homogeneous solution, the P3HT solution was poured into ZnO solution and the ultrasonicated again for 15 minutes to form well

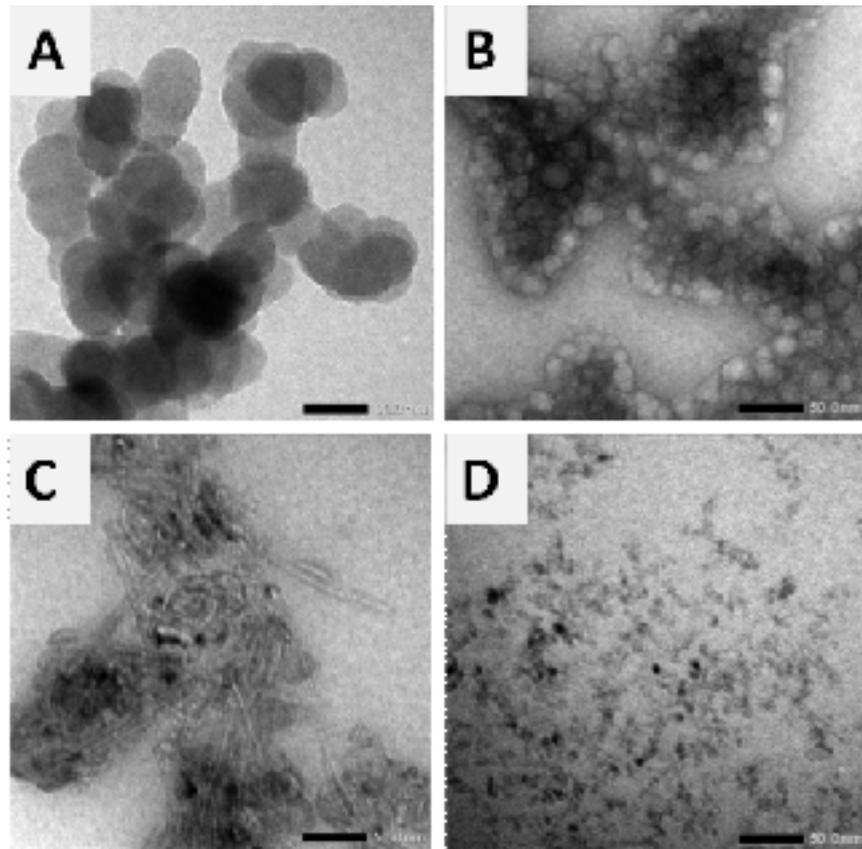


Figure 1: TEM images of (a).ZnO-NP, (b).SQ-capped ZnO-NP, (c). 2-NT-capped ZnO-NP and (d).PVP-capped ZnO-NP. The scale bar is 50 nm.

mixed P3HT:cappedZnO-NP solution. All films were thermally annealed at 150°C for 60 minutes.

PIA spectra were measured on an FTIR spectrometer (FTS-7000, Varian) equipped with an MCT detector by using the different spectrum method [6]. Thin film of P3HT:capped ZnO nanoparticles put in the cold head of a cryostat (Oxford Instruments DN1754) under vacuum. The film was irradiated with 532-nm continuous-wave laser. The PIA spectra were measured the temperature range from 78 to 300 K by using a controller (Oxford Instruments ITC502S).

3. Results and Discussion

Fig. 1 shows TEM images of highly diluted ZnO-NP in methanol and ZnO-NP capped by SQ, 2-NT molecules and PVP polymer. The concentration of pristine and capped ZnO-NPs can not precisely determined. We diluted them until UV-Vis optical absorbance less than of the solutions is reached. The average diameter of ZnO-NP is 40 nm. Capping by SQ and 2-NT can clearly cover the surface of ZnO-NP as shown with bright images in Fig. 1(b) and (c). However, the effect of capping ZnO-NP by PVP polymer was unclear which might be caused by too large size of PVP. These results show that capping process by small molecules was successfully carried out.

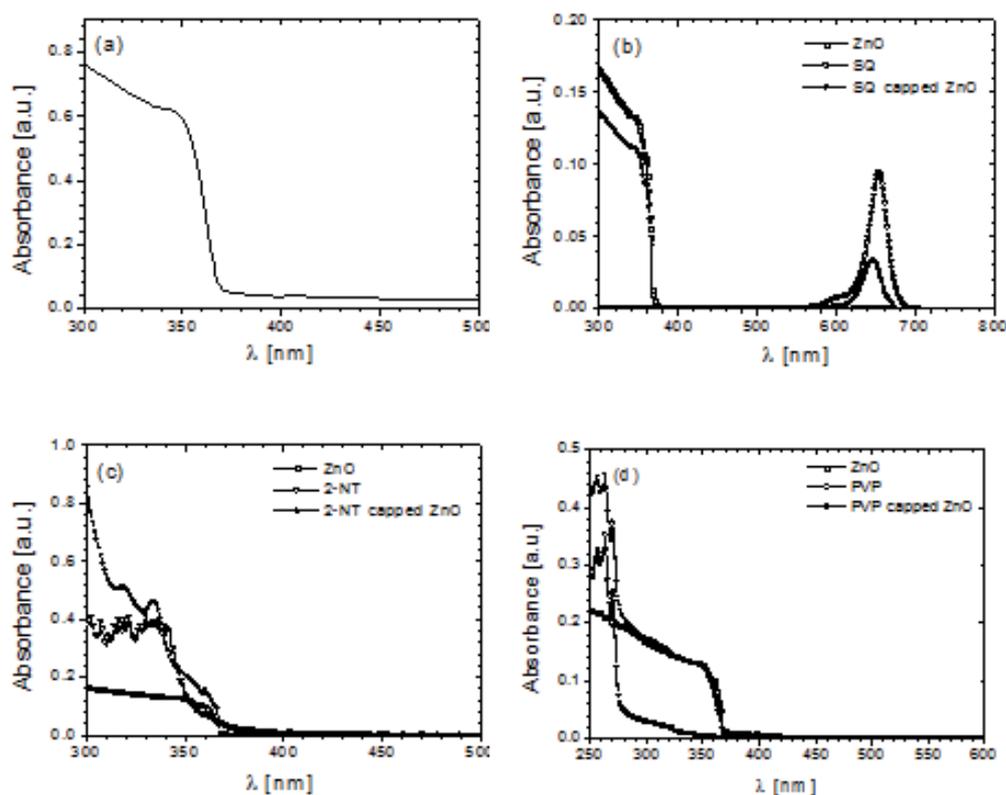


Figure 2: Absorbance spectra of (a).ZnO-NP in methanol, (b).ZnO-NP, SQ and SQcapped ZnO-NP, (c). ZnO-NP, 2-NT and 2-NTcapped ZnO-NP, (d). ZnO-NPs, PVP and PVPcapped ZnO-NP.

The optical absorbance of highly diluted solution of ZnO-NP, capping agents and ZnO capped by SQ, 2-NT and PVP are displayed in Figure 2(a)-(d). The ZnO-NP has absorption at wavelength below than 370 nm. The calculated optical bandgap of ZnO nanoparticle is 3.38 eV which is higher than that of its bulk (3.37 eV). It indicates that the synthesized ZnO forms nanoparticles as confirmed by TEM image of ZnO-NP with average diameter of 40 nm. Absorption spectra of capped ZnO nanoparticles clearly consist of the optical absorption of capping agent and ZnO-NP. This shows that capping agents can cover the ZnO nanoparticles as also confirm by TEM image displayed in Fig. 1(b) and (c). However, the effect of PVP capping on ZnO-NP can not be observed in TEM image as displayed in Fig. 1(d).

PIA spectra of blend films P3HT:ZnO-NP and P3HT:capped ZnO-NP measured at 77 K are displayed in Fig. 3. The observed spectra exhibit complicated features which are attributed to the interaction between an electronic transition and vibrational transitions of photogenerated carriers. The band at 1256 cm^{-1} is well-known assigned due to positive polaron contribution [8]. The difference absorbance (ΔA) at 1240 cm^{-1} and 1450 cm^{-1} was used as the intensity of the polaron absorption was applied to determine the activation energy of charge carriers recombination process.

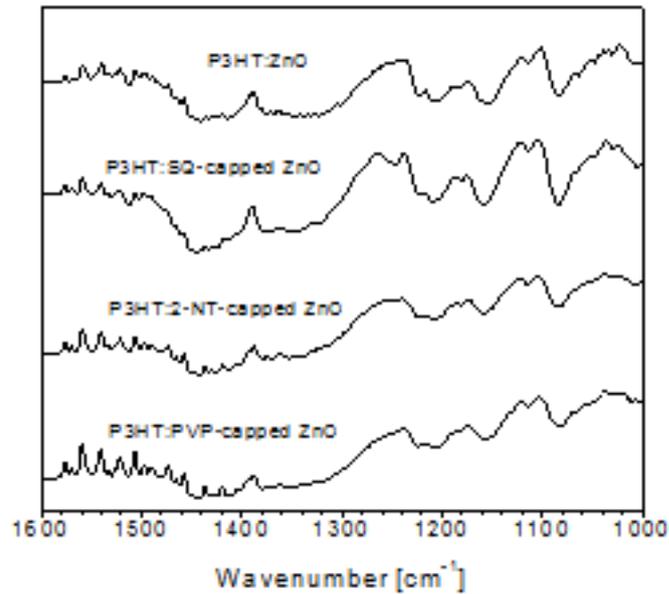


Figure 3: PIA spectra of P3HT:ZnO-NP and P3HT:capped ZnO-NP at 77 K.

The recombination dynamics of photogenerated carriers can be simply expressed by [6]:

$$\frac{d[P]}{dt} = \phi F - k_r [P][N] \tag{1}$$

where F is the rate of the formation of the excited states in P3HT:ZnO-NP film; ϕ is the effective efficiency of charge separation; [P] and [N] are the concentrations of positive carriers (positive polaron) and negative carriers (the anion), respectively and k_r is the carrier recombination rate. By assuming that the number of positive and negative carriers is equal, the absorbance due to positive polaron can be defined by $\Delta A = \sigma [P]$, where σ is the absorption cross-section of the band. By assuming that recombination rate can be expressed by the Arrhenius-type activation energy:

$$k_r = C \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{2}$$

where k_B is Boltzmann's constant and T is temperature. The relation between difference absorbance and activation energy (ΔE) caused by carriers recombination is:

$$\ln \frac{1}{(\Delta A)^2} = -\left(\frac{\Delta E}{k_B T}\right) + \ln \frac{C}{\phi F \sigma^2 l^2} \tag{3}$$

where l is the thickness of the film.

The plots of $\ln(1/(\Delta A)^2)$ versus $1/T$ plots (Arrhenius plot) of films are displayed in Fig. 4. The data can be considered as two straight lines ranging from low temperature of 78 to 120 K and high temperature of 140 to 300 K. A deflection point is observed at around 130 K. These data shows the existence of two parallel recombination processes of positive and negative carriers.

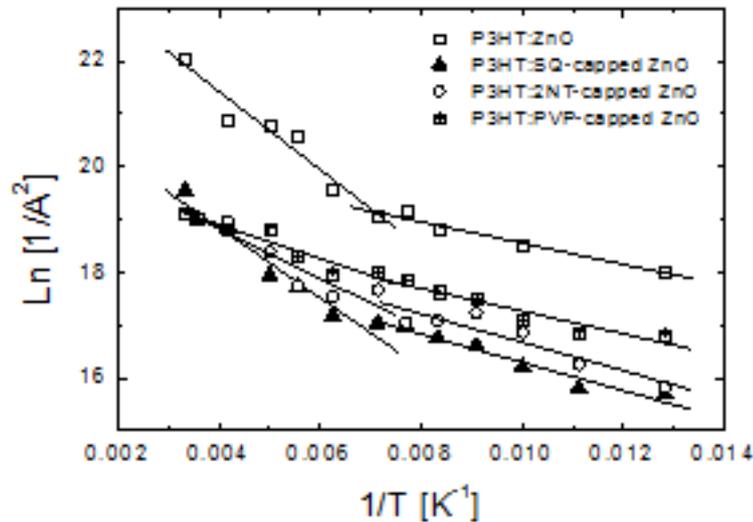


Figure 4: Plot of $\ln(1/\sigma A^2)$ versus $1/T$ of all films. The lines were determined by least squares method.

The activation energies at low and high temperatures for all films are listed in Table 1. For P3HT:ZnO-NP uncapped film, the activation energy σE at low temperatures (78-120 K) is 17 meV, while at high temperature (140-300 K) is 64 meV. The different value of activation energy can be explained by the existence of two types of positive polaron motion in the film. The low activation energy is attributed to polaron motion along polymer chain, whereas the higher activation energy to polaron motion from one chain to another polymer chains or inter-chain motion [9]. The polaron motion from one P3HT-chain to another P3HT chains is natural properties of charge carriers mobility in the polymer that strongly depend on temperature. Thus the intra- and inter-chain polaron motion correlates strongly with performance of a solar cell.

The activation energies at low temperature of all samples are almost equal around 20 meV. This indicates that the energy required for positive polaron moves along P3HT chain is not influenced by capping agents. Similar value is also obtained from films of P3HT:PCBM and P3HT:10%ZnO-NP:PCBM as reported in our previous work [7]. A significant change of σE is observed at high temperature. The inter-chain polaron motion is strongly affected by capping agents. The activation energy is decreased from 57 to 40 and 28 meV when the ZnO nanoparticles are capped by small molecules squaraine (SQ), 2-naphthalene (2-NT) and polymer PVP, respectively, which might be related to the molecular size of the capping agents. The molecular size is increased from SQ to 2-NT and PVP, thus larger molecular size of capping agents facilitate positive polaron easier to move from one P3HT-chain to another P3HT-chain (interchain). Based on the value of activation energy at high temperatures, the PVP-capped ZnO-NP can expected to improve the performance of hybrid P3HT:ZnO-NP solar cells due to the easy of polaron to move to another P3HT-chain and can reach the anode and finally produce electricity.

Sample	ΔE at low T (meV)	ΔE at high T (meV)
P ₃ HT:ZnO-NP	17±2	64±2
P ₃ HT:SQcapped ZnO-NP	23±5	57±6
P ₃ HT:zNTcapped ZnO-NP	23±6	40±13
P ₃ HT:PVPcapped ZnO-NP	19±3	28±17

TABLE 1: Activation energy ΔE determined from PIA measurement.

4. Conclusions

The photogenerated charge carriers motion in the blend films of P₃HT:ZnO-NP and P₃HT:capped ZnO-NP were investigated by use of PIA spectroscopy at various temperature from 78 to 300K. The activation energy that obtained from PIA measurement at low temperatures and high temperatures are related to the positive carrier motion along P₃HT chain or intra-chain and inter-chain, respectively. The intra-chain polaron motion is not influenced by the capping agents, while the inter-chain motion strongly depends on capping agents due to the difference of their molecular size.

5. Acknowledgement

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