Improved charge carrier transfer in squaraine-capped ZnO nanoparticles layer for electron transport of hybrid solar cells

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Abstract. Blend of conjugated polymer poly(3-hexylthiophene) or P3HT and Zinc Oxide nanoparticles (ZnO-NPs) has been intensively used as active material for high performance hybrid solar cells. However, agglomeration of ZnO-NPs hinders efficient charge carrier or charge transfer both from P3HT to ZnO-NPs and its transport within ZnO-NPs which lead to low performance of solar cells. Capping of ZnO-NPs is currently applied to avoid this agglomeration effect. In this study, we used small molecule squaraine (SQ) to cap ZnO-NPs. SQ was chosen due to its lowest unoccupied molecular orbital (LUMO) level lower than conduction band of ZnO, therefore, SQ can assist charge transfer to ZnO-NPs. Moreover, SQ molecule also enhances light absorption due to its high light absorption in the near infrared region and large spectral overlap between the P3HT emission and SQ absorption. Here we report our current study on charge carrier transport in the blend of P3HT and SQ-capped ZnO-NPs by using photoluminescence spectroscopy with UV and blue excitation wavelengths. ZnO-NPs were synthesized by using sol-gel method. The capping process was employed by mixing small amount of SQ solution into the ZnO-NPs gel before its blend with P3HT. Small molecule SQ was successfully capped ZnO-NPs as observed from its TEM image. ZnO-NPs solution has absorption wavelength less than 380 nm, therefore, no emission spectrum is observed when it is excited with 473 nm excitation wavelength. However, a clear emission spectrum is observed from SQ-capped ZnO-NPs solution, which shows that charge transfer was occurred from SQ to ZnO-NPs. Similar behavior was also observed in the blend of P3HT and SQ-capped ZnO-NPs. Our study shows that small molecule squaraine can improve charge carrier transfer from ZnO-NPs and therefore the performance of solar cells might be increased.

1. Introduction

Hybrid organic-inorganic solar cells have been intensively studied to obtain high performance and low cost solar cells [1-4]. Combination of superior optoelectronic properties of inorganic materials and low-cost preparation methods of organic semiconducting molecules make hybrid organic-inorganic materials as promising materials for optoelectronic devices, such as diode and solar cells. Blend of conjugated polymers poly(3-hexylthiophene) or P3HT and zinc oxide nanoparticles (ZnO-NPs) has been recently developed for high performance solar cells. Combination of high hole mobility and versatile processing of P3HT and high electron mobility of ZnO-NPs is expected to produce high performance solar cells. Zinc oxide has also low exciton binding and its conduction band is lower than LUMO of P3HT which facilitates easier for charge transfer from excited electrons in P3HT into ZnO-NPs. Moreover ZnO-NPs can be synthesized at lower temperature which is suitable for mixing with conjugated polymers. Although several efforts have been done, the Power Conversion Efficiency...
(PCE) of hybrid solar cells is still below 2%, far below reported fully organic BHJ solar cells, like P3HT:fullerene indene-C60-bisadduct (ICBA) blend solar cells above 7% [5]. Oosterhout et al. [6-7] reported 2% PCE hybrid solar cells using control morphology of blend P3HT:ZnO films. The main problem of this low PCE is caused by the difficulty of morphology control of hybrid layer and the understanding of charge carrier motion or transport both in P3HT or in ZnO, which is still not fully revealed yet [8]. The low PCE of P3HT:ZnO nanoparticles is mainly caused by the difficulty of morphology control of hybrid layer, especially in controlling aggregation of ZnO nanoparticles. Agglomeration or aggregation of ZnO-NPs forming large size particles will decrease its surface area and hinders charge transport from P3HT to ZnO, thus lowers the performance of solar cells. Capping ZnO nanoparticles with small molecules and polymers is therefore commonly used to avoid the agglomeration in ZnO-NPs.

Recently, several groups have used small semiconducting molecules or surfactants such as naphthalene [9], pyridine [10] and fullerene derivative PCBA [11] to overcome ZnO agglomeration and have successfully increased the electric current and PCE of hybrid solar cells. Li et al. studied theoretically hybrid P3HT:ZnO nanoparticles capped with monolayer of fullerene derivative PCBA [11]. They found that the external quantum efficiency (EQE) of hybrid P3HT:ZnO solar cells can be tripled due to induced interfacial dipole and shifted-up the LUMO level of P3HT relative to the conduction band edge of ZnO. Therefore, the capping molecules should possess high electron mobility and suitable LUMO level both with ZnO and P3HT to facilitate more charge transfer, thus finally to increase the PCE of solar cells.

In this study, we used small molecules squaraine (SQ) to cap ZnO nanoparticles. The intense absorption and emission property of squaraine, which is associated with the strong charge-transfer interaction, is ideally suited for applications related to the photosensitization phenomenon. Squarine absorption bands with the extinction coefficient of ~ 10^5 L mol^{-1}cm^{-1} generally become rather broad in the solid state near the IR region and photostable as a consequence of the strong charge transfer or intermolecular interactions and a tendency to aggregation. Recently, it has been reported a near infrared light-emitting field-effect transistor based on squaraine compounds with relative balance electron and hole mobilities in the order of 10^{-4} cm^{2}/Vs [12]. Moreover, the hole mobility increases up to 10^{-3} cm^{2}/Vs as the devices are thermally annealed. The PCE of SQ:fullerene solar cells have reached more than 6% [13]. The highest occupied molecular orbital (HOMO) and LUMO levels of SQ are -5.3 eV and -3.6 eV, respectively [14] which are lower than that of P3HT (-5.1 eV and -3.1 eV) [15]. The most important parameter for capping is the LUMO of SQ, which is higher than the Conduction Band (CB) of ZnO at -4.2 eV. Therefore, capping ZnO-NPs using squaraine is expected not only to avoid agglomeration of ZnO-NPs, but also to improve charge transfer from P3HT to ZnO-NPs, thus the PCE of solar cell can be increased.

2. Materials and Experimental Methods
2.1. Materials and Samples Preparation
Conjugated polymer P3HT, small molecule SQ, methanol and chlorobenzene were purchased from Sigma Aldrich. Chemical structure of P3HT and SQ are shown in figure 1. Zinc acetate dehydrate and sodium hydroxide were purchased from Merck. All materials are used as received without any further purification. ZnO nanoparticle was synthesized using sol-gel method, as described in our previous work [16].

The ZnO-NPs solution was prepared by dissolving ZnO nanoparticles gel in methanol. Squaraine was dissolved in methanol. Capping of ZnO-NPs by SQ was prepared by mixing ZnO-NPs solution and few drop of SQ solution and then was ultrasonicated for 15 minutes to obtain the homogeneous solution. Meanwhile the blend of P3HT:ZnO-NPs, P3HT:SQ and P3HT:ZnO-NPs:SQ were dissolved in chlorobenzene.
2.2. Characterization

The particle sizes of ZnO-NPs and SQ-capped ZnO-NPs were measured by use of Transmission Electron Microscopy (TEM JEOL JEM 1400). The optical absorption of each solution and their blend were measured by use of T70+UV-Vis spectrometer. In order to study charge carrier transfer from SQ into ZnO-NPs, the photoluminescence (PL) of uncapped ZnO-NPs solution and SQ-capped ZnO-NPs solution were performed by fluorometer with excitation wavelength of 325 nm (UV-light) and 473 nm (blue light). We also measured the PL spectra of blend solution of P3HT:ZnO-NPs, P3HT:SQ and P3HT:SQ:ZnO-NPs.

3. Results and Discussion

Figure 2 shows TEM images of uncapped-ZnO-NPs and SQ-capped ZnO-NPs diluted solution in methanol. The average diameter of ZnO-NPs is 40 nm. Agglomeration is still can clearly observed even in a much diluted solution. Capping molecule SQ covers the surface of ZnO-NPs as shown with bright images of smaller particles than ZnO-NPs. This results show that capping process was successfully carried out, although agglomeration of ZnO-NPs is still preserved. The capping mechanism of SQ molecules into ZnO-NPs is still unclear, whether due to chemically bonding of SQ molecules to hydroxyl groups of ZnO-NPs or mechanically bonding. The different size of ZnO-NP between uncapped-ZnO-NP and SQ-capped-ZnO-NPs is caused by agglomeration during synthesis.

UV-Vis absorption spectra of ZnO-NPs, SQ and SQ-capped ZnO-NPs solutions are shown in figure 3. ZnO-NPs absorb light at wavelengths shorter than 370 nm, with wavelength cut-off at 369 nm, while SQ solution absorbs at longer wavelengths ranging from 620 nm to 680 nm. We calculated the optical bandgap of ZnO nanoparticle from wavelength cut-off and obtained 3.38 eV. This value is higher than that of its bulk (3.37 eV), which indicates that the synthesized ZnO forms nanoparticles as confirmed by TEM image of ZnO-NPs with average diameter of 40 nm. Absorption spectra of SQ-capped ZnO-NPs clearly consist of the optical absorption of SQ molecule and ZnO-NPs. This shows that SQ can cover or cap the ZnO-NPs as also confirmed by TEM image displayed in figure 2.
Figure 3. UV-Vis spectra of ZnO-NPs, SQ and SQ-capped ZnO-NPs solutions in methanol.

PL spectra of ZnO-NPs, SQ and SQ-capped ZnO-NPs are displayed in figure 4(a). For comparison, their absorption spectra are also displayed in the figure. The excitation wavelength is 325 nm (UV-light). Two PL peaks are observed in ZnO-NPs solution related to the intrinsic defect at 3.22 eV (Zinc vacancy or UV emission) and at 2.32 eV related to the interstitial zinc defect [17]. The defect at 1.62 eV which is caused by oxygen vacancy [17] is not observed due to overlap with the second generation of excitation wavelength (650 nm) as shown by huge peak intensity in PL spectra. The processes of absorption and photoluminescence in ZnO-NPs are energetically illustrated in figure 4(b).

Figure 4. Photoluminescence spectra of (a) ZnO-NPs, SQ-capped ZnO-NPs and (b) Schematic process of absorption and emission in ZnO-NPs. The excitation wavelength is 325 nm.

In order to study the effect of SQ to the charge transfer, we measured PL spectra of uncapped and SQ-capped ZnO-NPs. Their PL spectra are shown in figure 5(a). No emission of ZnO-NPs is observed when excited by 473 nm. This can be easily understood because the excitation energy is smaller than the energy gap of ZnO-NPs, therefore the required energy for charge to be excited into conduction band of ZnO is not sufficient. Meanwhile, the SQ molecules exhibit PL emission peak at 700 nm, which shows that the energy gap is 1.7 eV. This energy gap is similar to the difference between HUMO and LUMO level of SQ (1.7 eV) as mention above.

Photoluminescence spectrum of SQ-capped ZnO-NPs solution as shown in figure 5(a), however, shows a significant PL peak at wavelength around 600 nm. By using the excitation wavelength at 473 nm, the emission of excited electron is not possible to take place in ZnO-NPs due to insufficient energy. Therefore, this PL peak is clearly caused by charge transfer from SQ molecules to ZnO-NPs and then subsequently emitted in ZnO-NPs. This result shows that small molecule SQ assists more
charge transfer to ZnO nanoparticle through Forster Resonance Energy Transfer (FRET) process [18]. The charge transfer processes in SQ-capped ZnO-NPs can be schematically illustrated in figure 5(b).

Figure 5. Photoluminescence spectra of (a) ZnO-NPs, SQ-capped ZnO-NPs and (b) Schematic process of absorption and emission in SQ-capped ZnO-NPs. The excitation wavelength is 473 nm.

Figure 6 shows the PL spectra of blend solution of P3HT, P3HT:ZnO-NPs, P3HT:SQ and ternary P3HT:SQ-capped ZnO-NPs. The PL of P3HT shows broad spectrum with a strong peak at 584 nm, corresponds to energy gap of 2.12 eV, which is close to the difference value of HUMO (-5.1 eV) and LUMO level (-3.1 eV) of P3HT [15]. The broad spectrum of PL indicates the broad of energy bands or energy levels both in HUMO and LUMO levels. A shoulder PL peak at 626 nm is attributed to aggregation of P3HT chains [19-21]. Blend hybrid P3HT:ZnO-NPs solution has similar PL spectrum with P3HT only, which shows no observed charge transfer occurs from P3HT into ZnO-NPs. Other study showed that the charge transfer from P3HT chains to ZnO-NPs can be observed in PL spectra of P3HT:ZnO-NPs blend solution by varying the ZnO-NPs concentration. The decreased of PL spectra with the increased of ZnO-NPs concentration indicates the charge transfer is occurred from P3HT to ZnO-NPs [2].

The PL spectrum of P3HT:SQ solution shows two distinguished peaks at 567 nm and at 696 nm. The first peak is assigned to emission in P3HT and the second strong peak is attributed to the emission peak in SQ molecules. We cannot clearly observe the charge transfer from P3HT chains to the SQ molecules. In the solution of P3HT:SQ-capped ZnO-NPs, three PL peaks are observed. The first peak at 567 nm is due to emission in P3HT, the second peak is caused by the emission in ZnO-NPs. The clear distinguished peak at 675 nm is clearly attributed to the emission in SQ molecules. Again, however, it is very difficult to distinguish charge transfer from P3HT to ZnO-NPs and to SQ molecules or from SQ molecules to ZnO-NPs due to strong overlap of their PL emission spectra. Additional time resolved photoluminescence spectroscopy is therefore highly required to clarify the effect of SQ into charge transfer in the blend of P3HT:SQ-capped ZnO-NPs. However, from figure 5, it is clearly confirmed that SQ molecules facilitate more charge transfer from SQ to ZnO-NPs.
Figure 6. Photoluminescence spectra of solutions of P3HT, blend P3HT:ZnO-NPs, P3HT:SQ and ternary P3HT:SQ-capped ZnO-NPs (P3HT:ZnO-NPs/SQ). The excitation wavelength is 473 nm.

4. Conclusion
We have successfully synthesized ZnO-NPs with average diameter of 40 nm and capped ZnO-NPs by small molecule squaraine. The SQ molecules facilitate charge transfer from SQ into ZnO-NPs as confirmed by the appearance of PL peak even though if it was excited with photon energy smaller than bandgap of ZnO-NPs. We believe that by capping ZnO-NPs with SQ molecules, the performance of hybrid P3HT:ZnO-NPs solar cells can be improved due to the enhanced charge transfer from SQ to ZnO-NPs.

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