The investigation of current-voltage characteristics based on poly(2-methoxy,5-octoxy)-1,4-phenylenevinylene-PbSe composite solar cells

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Abstract. A bulk heterojunction photovoltaic device was prepared based on the blend of conjugated poly[(2-methoxy,5-octoxy)-1,4-phenylenevinylene] (MOPPV)-inorganic PbSe quantum dots. We studied the device performance of the active layer with different mass ratio, and the device performance was best when PbSe wt% was 50% in the MOPPV-PbSe composites, as well as, the short-current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$) and the power conversion efficiency ($\eta$) of the device were 3.661mA/cm$^2$, 0.326V, 23% and 0.277%, respectively. Results indicated that PbSe quantum dots in composite was helped to exciton dissociation, charge transfer, and mobility.

1. Introduction

Recently, conjugated polymer-semiconductor quantum dots(QDs) composites devices based on organic-inorganic hybrid materials have been improved significantly in power conversion efficiency. Conjugated polymer materials have excellent flexibility, machinability and low-cost, so they attracted great attention[1-4]. Hybrid photovoltaic devices take advantages of both organic and inorganic semiconducting materials[5-8]. First, because of high carrier mobilities of QDs, the exciton dissociation efficiency and the electron transport efficiency are enhanced. Besides, the band gap of QDs is tunable, so, the range of absorption spectrum of the composites structure can extend from the ultraviolet to the infrared, which can enhance optical absorption. Last, low band gap polymers also make them more optical absorption. Midgett et al[9,10], reported multiple exciton generation for different diameter PbSe QDs and different photo energies. They discovered that different PbSe QDs samples have different long-lived states.Yiyu et al[11], have fabricated a photovoltaic device based on MOPPV-MWNT:PCBM/PbSe, and the power conversion efficiencies can reach 0.4%. Wanli et al[12], investigated PbSe Schottky solar cells based on different PbSe quantum dots size, and they found when the diameter of PbSe was 2.3nm, the performance of solar cell was best, so the short-current density($J_{sc}$) is 17.2mA/cm$^2$, the open-circuit voltage($V_{oc}$) is 0.47V, the fill factor($FF$) is 0.57, and the power conversion efficiency($\eta$) is 4.57%. However, very few studies have been detailed reported for the blend of polymer-PbSe as the active layer solar cells.

PbSe QDs are II–VI semiconductors which the band gap is 0.26eV. So far, many polymer-semiconductor materials were investigated. Because of the nano-size effect of quantum dots, when PbSe QDs materials were incorporated into polymer materials MOPPV, it can form a intermediate band between LUMO band and HOMO band of MOPPV. The composites materials not only absorb photon which its energy much bigger than band gap of MOPPV, but also absorb photon...
which its energy smaller than band gap of MOPPV, which can absorb more photons to generate more
electron- hole pairs. So, PbSe nanocrystals show stronger quantum confinement[13]. The optical index
of PbSe quantum dots is much big, the infractive index is about 4.6, and the band gap of PbSe is
located in middle infrared and visible region[14,15]. With quantum size effect, PbSe QDs have
bandwidth absorption spectrum, which can enhance light absorption[1].

In this study, we synthesized PbSe quantum dots, then PbSe QDs materials were incorporated into
dossier materials, poly[(2-methoxy,5-octoxy)-1,4-phenylenevinylene](MOPPV), and MOPPV-PbSe
heterojunction devices were prepared with different mass ratio. The basic solar cells structure was
ITO/PEDOT:PSS/MOPPV-PbSe/LiF/Al, then we measured $J-V$ characteristic curve, at last, we studied
solar cells performance when the annealing temperature was 180°C for 2h. We found that PbSe QDs
have excellent dispersions in composites which can increase interface and contact areas, and it is in favor
of exciton dissociation and charge transport. So, PbSe quantum dots may be the best choice as electron
acceptors in polymer-semiconductor solar cells.

2. Experiment

The PbSe QDs were prepared in our laboratory[16,17]. First, Se powder and sodium
borohydride(mass ratio is 1.04:1) were putted into there-necked bottles, then put excess distilled water
and Ar, keep for 30min. Secondly, Pb(CH$_3$COO)$_2$ and excess mercapto propionic acid(MPA)
were putted into distilled water, and regulate the PH is 8.0 with NaOH, then put NaHSe into it under Ar
atmosphere, heating at 80°C, reflux about 2h, natural cooling to room temperature. Finally, in order to
get purer precipitate, it
was washed three times at least. The ultimate products was baked in vacuum drying oven. Individual
conjugated polymer MOPPV was synthesized by in situ polymerization method[18,19].

The devices structure was shown in Figure.1. The glass was treated as substrate, which was cleaned
in ultrasonic cleaner. The indium tin oxide(ITO) layer (with square resistance ~15Ω sq$^{-1}$) was prepared
by spin-coated, and the thickness of ITO was about 100nm. The Poly(3,4- ethylenedioxythiophene):
poly(styrenesulfonate) (PEDOT:PSS) layer was spin-coated on the top of ITO and roast at 100°C for
5h. Afterwards, the active layer MOPPV-PbSe nanocomposite with different mass ratio was
spin-coated from tetrahydrofuran solution about 150nm thin film, annealing at 100°C for 60min, then
LiF(~15nm) and Al(~120nm) were deposited on the top of MOPPV-PbSe layer which the
vacuum pressure was 2.0×10$^{-4}$Pa by physical vapor deposition (PVD), respectively. Finally, the
annealing temperature of the device was 180°C for 2h under vacuum condition[20]. The active area of
device is about 1cm$^2$.

![Figure 1. Schematic layout of MOPPV-PbSe hybrid photovoltaic device](image)

In this study, we use X-ray diffraction(XRD), atomic force microscope(AFM) and scanning
electron microscope(SEM) to measured structure and the microstructure of PbSe nanoparticles,
respectively. Meanwhile, we use JASCO V550 to measure ultraviolet-visible-near infrared absorption
spectra of PbSe QDs, MOPPV, and MOPPV-PbSe composites film. Besides, we used a solar simulator to investigate the current density-voltage (J-V) characteristics of the MOPPV-PbSe devices.

3. Results and discussion

Figure 2(a) shows the X-ray diffraction (XRD) pattern of PbSe film which was prepared by a colloidal chemical method. From the figure, we can see that there are eight diffraction peaks: 2θ=25.12°, 29.03°, 41.69°, 49.29°, 51.60°, 60.57°, 68.41°, 76.26°, then compare with the standard cards, we can attribute them to the cubic phase of the PbSe nanocrystals (111), (200), (220), (311), (222), (400), (420) and (422). This XRD pattern is consistent with the standard spectrum of PbSe, so we confirm that the product is PbSe nanocrystal. The microstructure of PbSe QDs was measured transmission electron micrograph (TEM) in figure 2(b). From the images, we can confirm the size of the nanoparticles by TEM analysis. The diameter of PbSe QDs was about 10nm (Figure.2(b), insert), and it was a nearly uniform spherical.

![Figure 2. (a) XRD pattern of PbSe QDs (b)TEM image of PbSe QDs.png](image)

Figure 2. (a) XRD pattern of PbSe QDs  (b)TEM image of PbSe QDs

Figure 3. Absorption spectra of PbSe QDs, MOPPV, and MOPPV-PbSe composites film

The ultraviolet-visible-near infrared (UV-vis-NIR) absorption spectra of PbSe QDs (circles), MOPPV (triangles), MOPPV-PbSe (squares) composites film were shown in Figure 3 at room temperature. Obviously, the maximum absorption peak of MOPPV-PbSe composites is 531nm, and the absorption peak of the composite has a red shift by about 40nm, compared to the pristine polymer
MOPPV. Because of the formation of intermediate band when PbSe QDs materials were incorporated into polymer materials MOPPV, the range of absorption spectrum was extended.

Figure 4. (a) SEM and (b) AFM images of the MOPPV-PbSe composites film

The SEM and AFM images of the MOPPV-PbSe composites film were shown in figure 4 (a) and 4(b). From the figure 4, we can see that the bright areas is Pbse QDs, and the darkest areas is MOPPV polymer materials. The results showed that PbSe QDs has excellent dispersion in composites. The MOPPV-PbSe composites provide excellent contact area, which enhances the exciton dissociation efficiency. Meanwhile they provide an effective transmission channel for charge transfer and transport, which can enhance the photovoltaic performance of devices.

To characterize devices performance, the MOPPV-PbSe solar cells device with the structure of Glass/ITO/PEDOT:PSS/MOPPV-PbSe/LiF/Al was fabricated, which PbSe QDs materials were incorporated into polymer materials MOPPV as active layer with different PbSe wt% from 10% to 90%. Then ,we used a solar simulator to investigate the current density-voltage(J-V) characteristics of the MOPPV-PbSe devices. The performce parameters of devices in different PbSe wt% such as $J_{sc}$, $V_{oc}$, $FF$, and $\eta$ were measured under 100mw/cm$^2$ illuminations in Table1. Obviously, the device performance was best when PbSe wt% was 50% in the MOPPV-PbSe composites, so at this time, $J_{sc}$ is 3.661mA/cm$^2$, $V_{oc}$ is 0.326V, $FF$ is 0.23, and $\eta$ is 0.277%. The results are represented in figure 5 below, when PbSe wt% was 50%, the values of $V_{oc}$, $J_{sc}$ and $\eta$ were the highest.

Table 1. Performce parameters of devices in different PbSe wt%.

| PbSe wt% | $V_{oc}$ (mV) | $J_{sc}$(mA/cm$^2$) | $FF$ | $\eta$ (%) |
|----------|---------------|---------------------|------|-------------|
| 10%      | 55.9          | 1.451               | 0.272| 0.022       |
| 20%      | 238.2         | 1.687               | 0.246| 0.099       |
| 30%      | 321.4         | 2.299               | 0.229| 0.169       |
| 40%      | 285.7         | 3.459               | 0.237| 0.234       |
| 50%      | 326.4         | 3.661               | 0.232| 0.277       |
| 60%      | 216.5         | 1.486               | 0.267| 0.086       |
| 70%      | 191.5         | 1.276               | 0.261| 0.064       |
| 80%      | 207.6         | 1.290               | 0.256| 0.067       |
| 90%      | 281.3         | 2.05                | 0.223| 0.128       |
Figure 6 shows the band energy diagram for ITO/PEDOT:PSS/MOPPV-PbSe/LiF/Al device. The favorable energy band of the device is in favor of exciton dissociation, charge transfer and collection. At the interface of MOPPV-PbSe materials, excitons in MOPPV are dissociated to electrons and holes because of barrier effect. Electrons are transferred efficiently from MOPPV to PbSe, then to LiF, at last they are collected by the Al electrode, meanwhile holes are transferred efficiently from MOPPV to PEDOT:PSS, to ITO. With high carrier mobility and low band gap of PbSe QDs in MOPPV, electrons are easily transferred from LUMO of MOPPV to conduction band of PbSe. The device provides continuous transport pathway separately for electrons and holes before they are recombined.

4. Conclusion
In summary, the perforce parameters of devices with different PbSe wt% in MOPPV-PbSe composite system were investigated systematically in this study. The device performance was best when the PbSe wt% was 50% in the MOPPV-PbSe composites, so at this time, the short-current density is 3.661 mA/cm², the open-circuit voltage is 0.326 V, the fill factor is 0.23, and the power conversion efficiency is 0.277%.
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