Improved performance of perovskite photodetectors with a hybrid planar-mixed heterojunction

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Supplementary material for this article is available online

Keywords: perovskite photodetector, heterojunction, grain boundary, electron transfer

Abstract

Improved performance of lateral perovskite photodetectors is demonstrated based on a hybrid planar-mixed heterojunction structure, which comprises a CH3NH3PbI3:PC61BM (6,6-phenyl-C61-butyric acid methyl ester) bulk heterojunction on a planar SnO2 layer. The photodetector with an optimized PC61BM doping concentration shows a photocurrent more than three times to that device without a PC61BM doping or without a planar SnO2 layer, confirming that the hybrid planar-mixed heterojunction structure plays an important role in improving the performance of the devices. The photodetector exhibits a responsivity higher than 2 A W−1 in a wide range from ultraviolet to near infrared with a maximum one of 9 A W−1 at 315 nm. The improved performance is not only attributed to the increased electron transporting ability and the dissociation probability of excitons and/or electron-hole pairs in perovskite, but also to the growth of compact perovskite films with decreased grain boundary and hence the increased charge carriers transporting efficiency due to the introduction of PC61BM.

1. Introduction

Organic/inorganic hybrid perovskites have emerged as the active materials for many optoelectronic devices, such as solar cells and light-emitting diodes, due to their merits of direct bandgap, large absorption coefficient, high carrier mobility, long exciton diffusion length, and compatible with various substrates [1–6]. Perovskite photodetectors, which have the potential applications in optical communications, environmental monitors, imaging, and chemical/biological sensing, have also attracted more and more attention since the first device demonstrated in 2014 [7–14]. From the structure point of view, there are typically two types perovskite photodetectors, e.g., vertical- and lateral-type devices. Compared with the vertical counterparts, the lateral photodetectors are easy to obtain a photocurrent gain because of the photoconduction working mechanism of these devices. Many strategies have been proposed to improve the performance of these photodetectors, one of which is to adopt a planar heterojunction structure. The materials that can be combined with perovskites to form such a planar heterojunction including two dimensional materials, organic, and inorganic semiconductors [15–21]. Similarly, a bulk heterojunction structure is also exploited [22–25]. Among the materials used in such a bulk heterojunction, [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) has gained the most attention [26–30]. On one hand, PC61BM can act as an electron acceptor that increases the dissociation efficiency of the photogenerated excitons or electron-hole pairs in the perovskites. On the other hand, it can passive the defect states in the perovskite grain boundary and increase the conductivity of the film, which compensates the lower diffusion length of electron compared to the hole one in the perovskite films [31–34].
In previous work, we have demonstrated that the performance of the perovskite photodetector can be improved with a CH$_3$NH$_3$PbI$_3$/SnO$_2$ planar heterojunction [35]. In this work, a hybrid planar-mixed heterojunction is adopted to further improve their performance. The hybrid planar–mixed heterojunction perovskite photodetectors comprise a CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM bulk heterojunction on a planar SnO$_2$ layer. The photodetector with an optimized PC$_{61}$BM doping concentration shows a photocurrent more than three times to that device without a PC$_{61}$BM doping or without a planar SnO$_2$ layer. Correspondingly, the optimized device exhibits a responsivity higher than 2 A W$^{-1}$ in a wide range from ultraviolet to near infrared with a maximum one of 9 A W$^{-1}$ at 315 nm. This work confirms that the hybrid planar–mixed heterojunction structure is effective in improving the performance of the lateral perovskite photodetectors.

2. Experimental details

The CH$_3$NH$_3$PbI$_3$ precursor solution was prepared by dissolving CH$_3$NH$_3$I and PbI$_2$ at 1:1 (0.162:0.462 g) equimolar ratio in 0.7 ml N,N-dimethylformamide and 0.3 ml dimethyl sulfoxide, and the solution was stirred for 12 hours at 70 °C before using. For the bulk heterojunction films, 0.05, 0.1, and 0.5 mg PC$_{61}$BM were added to the CH$_3$NH$_3$PbI$_3$ precursor solution, respectively, which formed different doping concentration of PC$_{61}$BM in CH$_3$NH$_3$PbI$_3$ films. The photodetectors were fabricated on ultraviolet–ozone treated glass substrates. Firstly, SnO$_2$ aqueous solution was spin-coated onto the pretreated glass substrates at a rate of 3000 rpm and then annealed at 150 °C for 30 min, which formed a SnO$_2$ layer of about 140 nm [35]. CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM bulk heterojunction films were then spin-coated on the SnO$_2$ layer from the CH$_3$NH$_3$PbI$_3$ precursor solution with a rate of 3000 rpm for 5 s and 3000 rpm for 60 s in sequence. After 20 s delay, 30 μl chlorobenzene was quickly added during the spin-coating procedure. The substrates were then annealed at 70 and 105 °C for 3 and 10 min, respectively. All the above processes were carried out in ambient conditions. Au electrodes were thermally deposited onto the CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM films with a rate of 2 Å s$^{-1}$ in a vacuum chamber at a pressure of ~5 × 10$^{-4}$ Pa through a shadow mask, defining the channel length and width of 1000 and 60 μm, respectively. The morphologies of the films were obtained on a Hitachi S4800 scanning electron microscopy (SEM). X-ray diffraction (XRD) pattern was measured with a Rigaku D/Max-2500 x-ray diffractometer using a Cu K$\alpha$ radiation (λ = 1.540 56 Å). Absorption spectra were recorded on a Shimadzu UV–3101PC spectrophotometer. The current–voltage (I–V) characteristics were measured using a Keithley 2400 sourcemeter. The external quantum efficiency (EQE) data was measured with a Stanford SR803 lock-in amplifier under monochromatic illumination at a chopping frequency of 130 Hz by a Stanford SR540 chopper, and the monochromatic lights were obtained from a monochromater under illumination of a 300 mW cm$^{-2}$ Xenon lamp. All measurements were performed under ambient conditions and at room temperature.

3. Results and discussion

The surface morphology of the CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM films on SnO$_2$ are shown in figure 1. From the SEM images with a lower amplification ratio (upper in figure 1), it can be found that there are some pin holes in the pristine CH$_3$NH$_3$PbI$_3$ film. The size of the pin holes decreases but the density increases in the 0.05 mg ml$^{-1}$ PC$_{61}$BM doped CH$_3$NH$_3$PbI$_3$ film. Further increase the concentration of PC$_{61}$BM results in decreases of both the size and density of the pin holes. From the SEM images with a larger amplification ratio (lower in figure 1), it can be found that the average grain size in the pristine CH$_3$NH$_3$PbI$_3$ film is about 300 nm. However, the average grain size in the 0.05 mg ml$^{-1}$ PC$_{61}$BM doped CH$_3$NH$_3$PbI$_3$ film is a little lower, but it increases with the doping concentration of PC$_{61}$BM and a size of about 300 nm in found in the 0.5 mg ml$^{-1}$ PC$_{61}$BM doped CH$_3$NH$_3$PbI$_3$ film. The compact morphology of the perovskite films doped with PC$_{61}$BM decreases the grain boundary and hence the decreased defect state density and increased charge carrier transporting efficiency. Meanwhile, the PC$_{61}$BM can also passivate the defect states and increase the conductivity of the perovskite films [31–34]. These properties indicate that hybrid planar–mixed heterojunction structure may be favorable in improving the performance of the lateral perovskite photodetectors.

Figure 2 illuminates the XRD patterns of the CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM films on SnO$_2$. The XRD pattern of the pristine CH$_3$NH$_3$PbI$_3$ film presents obvious diffraction peaks at 14.26°, 28.34°, and 32.02°, which originates from the reflections of (110), (220), and (310) crystal planes of CH$_3$NH$_3$PbI$_3$, respectively [36]. Similar diffraction peaks are found in the CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM films. However, a small diffraction peak of PbI$_2$ at 12.7° is found in the 0.5 mg ml$^{-1}$ PC$_{61}$BM doped CH$_3$NH$_3$PbI$_3$ film, suggesting that the PbI$_2$ is not fully converted to CH$_3$NH$_3$PbI$_3$ when a high concentration of PC$_{61}$BM is employed. This is attributed to the aggregation of PC$_{61}$BM at a higher concentration, which disturbs the growth dynamic of the perovskite film.

Figure 3 displays the I–V characteristics of the photodetectors under illumination of an AM 1.5G solar simulator with an intensity of 100 mW cm$^{-2}$. The structure of the photodetector is shown in the inset of figure 4.
Figure 1. SEM image of the CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM films on SnO$_2$ with a PC$_{61}$BM doping concentration of (a) 0, (b) 0.05, (c) 0.1, and (d) 0.5 mg ml$^{-1}$, (e)–(h) the corresponding films with a higher amplification ratio, and the scale bars in (a)–(d) are 2 μm and in (e)–(h) are 400 nm.

Figure 2. XRD patterns of the CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM films on SnO$_2$ with different PC$_{61}$BM doping concentrations.

Figure 3. I–V characteristics of the photodetectors under illumination of an AM 1.5G solar simulator with an intensity of 100 mW cm$^{-2}$, inset: device structure of the hybrid planar-mixed heterojunction photodetectors.
The CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM bulk heterojunction film on planar SnO$_2$ layer forms a hybrid planar–mixed heterojunction. All the photodetectors present a nearly linear I–V curves, suggesting an Ohmic contact between CH$_3$NH$_3$PbI$_3$ and Au electrodes. The photocurrent of the photodetector based on pristine CH$_3$NH$_3$PbI$_3$ is about 1.12 $\mu$A at 10 V. The photocurrent is dramatically increased for the photodetectors with CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM bulk heterojunction films. Among the photodetectors, the device with a 0.1 mg ml$^{-1}$ PC$_{61}$BM exhibits the highest photocurrent of 3.55 $\mu$A at 10 V, which is increased more than two times compared to the pristine CH$_3$NH$_3$PbI device. Besides, the dark current of the devices are all in the orders of 10$^{-9}$ A, which provides an ON/OFF ratio in the orders of 10$^3$.

The responsivity of the photodetectors can be extracted from their EQE spectra. Figure 5 reveals the responsivity of the photodetectors at 1 V. A broad band response is found for all the devices. The similar shape of the response spectra suggests that the excitons of PC$_{61}$BM contributes little to the photocurrent of the photodetectors, which may be attributed to its lower concentration. Among the photodetectors, the device with a 0.1 mg ml$^{-1}$ PC$_{61}$BM exhibits the highest responsivity in the whole response region, which is consistent to trend found in the I–V curves. Moreover, the responsivity is higher than 2 A W$^{-1}$ in the whole response region, and a maximum one of about 9 A W$^{-1}$ is obtained at 315 nm.

The response speed is another important figure-of-merit of a photodetector. Figure 6 shows the transient photocurrent of the optimized SnO$_2$/CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM photodetector at 1 V. The device was under illumination of a white light, and the light on and off were tuned by a SR540 optical chopper at a frequency of 12.5 Hz. The rise time is defined as the time for the photocurrent of the photodetector to reach 90% of its maximum value, while the decay time is for the photocurrent decreases to 10% of its maximum value. The rise and decay times of the optimized photodetector is about 10 and 8 ms, respectively. Such responses are comparable to our previous reported SnO$_2$/CH$_3$NH$_3$PbI$_3$ photodetector [35]. It should be noted that it needs a time for the chopper to open and block the light. However, this time is in the range of 0.1 to 0.2 ms that

![Figure 4](image1.png)

**Figure 4.** (a) Device structure of the hybrid planar–mixed heterojunction perovskite photodetectors, (b) schematic electron transfer in the photodetectors.

![Figure 5](image2.png)

**Figure 5.** Responsivity of the hybrid planar–mixed heterojunction photodetectors at 1 V.
calculated from the frequency of the optical chopper and of the size of the chopper blade. Comparing with the response times obtained from the transient photocurrent, such a time is significant shorter and can be ignored.

To understand the mechanisms for the improved performance of the hybrid planar-mixed heterojunction photodetectors, a photodetector with a 0.1 mg ml$^{-1}$ PC$_{61}$BM doped CH$_3$NH$_3$PbI$_3$ film on a glass substrate was also fabricated. Figure S1 is available online at stacks.iop.org/MRX/7/066201/mmedia shows the SEM images of the CH$_3$NH$_3$PbI$_3$PC$_{61}$BM film on glass substrate. A similar morphology with some pin-holes to that film on SnO$_2$ is found, which indicates that a limit contribution of the morphology to the improved performance of the photodetector. The XRD pattern shown in figure S2 reveals a small diffraction originated from PbI$_2$ at 12.7°, suggesting that small amount PbI$_2$ residual in the film. However, the photodetector based on this film shows a photocurrent of only 1 μA at 10 V under illumination of an AM 1.5G solar simulator with an intensity of 100 mW cm$^{-2}$ (figure S3). To reveal the absorption on the performance of the photodetectors, the absorption spectra of the CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM films on glass and SnO$_2$ are investigated, as shown in figure S4. Both the two films appear an absorption edge of about 780 nm, corresponding to a band-gap of 1.59 eV of CH$_3$NH$_3$PbI$_3$. The similar absorption of these two films rules out that the increased photocurrent of the hybrid planar-mixed heterojunction device is raised from the increased absorption. It should be noted that the contribution of the absorption of SnO$_2$ on the total absorption of the device can be ignored although SnO$_2$ has an absorption band at ultraviolet region, which is attributed to its significant lower absorption (in the orders of 10$^2$) compared with CH$_3$NH$_3$PbI$_3$ as demonstrated in our previous work [35]. As a result, the mechanisms of the improved performance of the hybrid planar-mixed heterojunction photodetectors can be explained as follows. On one hand, the PC$_{61}$BM in the hybrid planar-mixed heterojunction structure manipulates the growth of the CH$_3$NH$_3$PbI$_3$ films to form a more compact morphology with less grain boundary on SnO$_2$, which decreases the defect state density and increases the conductivity of the films. Besides, the PC$_{61}$BM can also passive the defect states in the CH$_3$NH$_3$PbI$_3$ grain boundary, which reduces the recombination probability of the photogenerated charge carriers. On the other hand, the SnO$_2$ and PC$_{61}$BM can also act as the electron acceptors for CH$_3$NH$_3$PbI$_3$. As shown in figure 5, the LUMO of CH$_3$NH$_3$PbI$_3$ is 3.9 eV, while they are 4.0 and 4.5 eV for PC$_{61}$BM and SnO$_2$, respectively. Thus electrons in CH$_3$NH$_3$PbI$_3$ can be effectively transfer to PC$_{61}$BM and SnO$_2$, which boost the dissociation efficiency of the excitons or electron-hole pairs formed in CH$_3$NH$_3$PbI$_3$ under illumination.

4. Conclusion

In conclusion, improved performance of the lateral perovskite photodetectors is demonstrated based on a hybrid planar-mixed heterojunction structure, which comprises a CH$_3$NH$_3$PbI$_3$:PC$_{61}$BM bulk heterojunction on a planar SnO$_2$ layer. The photodetector with an optimized PC$_{61}$BM doping concentration shows a responsivity of 9 A W$^{-1}$, which is more than three times to that device without a PC$_{61}$BM doping or a planar SnO$_2$ layer. It is found that the introductions of PC$_{61}$BM facilitates the growth of compact perovskite films and hence decreased the grain boundary, while the PC$_{61}$BM also passive the defect states in the CH$_3$NH$_3$PbI$_3$ grain boundary. These effects increase the conductivity of the devices. On the other hand, the SnO$_2$ and PC$_{61}$BM can act as the electron acceptors for CH$_3$NH$_3$PbI$_3$, which boosts the dissociation efficiency of the excitons or
electron-hole pairs formed in CH$_3$NH$_3$PbI$_3$ under illumination. These results confirm that the hybrid planar-mixed heterojunction structure plays an important role in improving the performance of the photodetectors. Such a structure may have potential applications in constructing high performance perovskite photodetectors.

**Acknowledgments**

This work was supported by the National Natural Science Foundation of China (61376062 and 61575192) and the Program for New Century Excellent Talents in Fujian Province University.

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