Ultrafast Responsive Non-Volatile Flash Photomemory Via Spatially Addressable Perovskite/Block Copolymer Composite Film

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Abstract

The exotic photophysical properties of organic-inorganic hybrid perovskite with long exciton lifetime and small binding energy have appeared as promising front-runners for next-generation non-volatile flash photomemory. However, the long photo-programming time of photomemory limits its application on light-fidelity (Li-Fi), which requires high storage capacity and short programming time. Herein, the spatially addressable perovskite in polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO)/perovskite composite film as photoactive floating gate was demonstrated to elucidate the effect of morphology on the photo-responsive characteristics of photomemory. The chelation between lead ion and PEO segment promoted the anti-solvent functionalities of perovskite/PS-b-PEO composite film, thus allowing the solution-processable poly(3-hexylthiophene-2,5-diyl) (P3HT) to act as the active channel. Through manipulating the interfacial area between perovskite and P3HT, ON/OFF current ratio of 10^4 and extremely low programming time of 5 ms can be achieved. This solution-processable and fast photo-programmable non-volatile flash photomemory can trigger the practical application on Li-Fi.

Keywords: floating-gate photomemory, perovskite, block copolymer, solvent annealing, multi-level memory

Introduction

Among the plethora of derivatives in optical communications, non-volatile flash photo-memory is of particular interest since it is the essential building block of computation technology for current big database storage device. Based on the similar principle of transistor-type memory which uses spatially-confined metallic or semiconducting floating-gate elements as charge-trapping site to electrically isolate trapped charges from the surrounding insulator, charge trapping/storing can be created using photon instead of electrical field. Large ON/OFF current ratio, long-term storage and short photo-programming time are essential to ensure the non-volatile flash photomemory as the substitute of electric-programming one. Yet, to date, there have been limited systematic studies of photomemory that address the photo-programming time for effective programming process. We demonstrate herein, for the first time, a non-volatile flash photomemory comprising an in-situ synthesis strategy of perovskite nanostructure in polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) as photo-active floating gate. The anti-solvent properties of PS-*b*-PEO/perovskite composite film make the solution-processable poly(3-hexylthiophene-2,5-diyl) (P3HT) as an active channel. The corresponding insulating/perovskite composite films were named as BCP-1/$MAPbBr_3$, BCP-2/$MAPbBr_3$, in the following.

Result and discussion

To investigate the interaction between $MAPbBr_3$ and PEO segmental matrix in the BCP, Fourier transform infrared spectroscopy (FTIR) spectra in the range of 650-4,000 cm^{-1} for $MAPbBr_3$, BCP-1 and BCP-1/$MAPbBr_3$ were performed Figure 1a.The peak for the stretching vibrations of the C-O bond shifted from 1,105.93 cm^{-1} in the pristine BCP film to 1,099.76 cm^{-1} in the BCP-1/$MAPbBr_3$ composite film. This shift reveals that the precursor Pb^{2+} ions preferentially coordinate with oxygen in the PEO unit of BCP via the Lewis acid–base interaction.

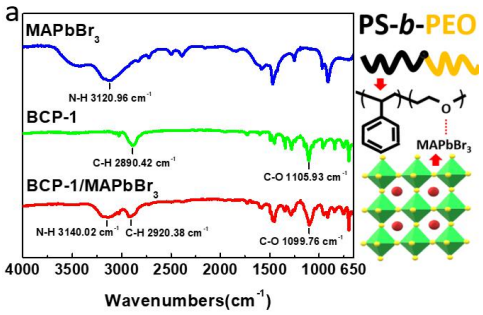

Figure 1. (a) FTIR spectra of the pristine BCP-1 and $MAPbBr_3$ and BCP-1/$MAPbBr_3$ composite film.

The perovskite-based photomemories were studied here and the device configuration with BCP/$MAPbBr_3$ composite film as photo-induced charge-trapping layer and P3HT as active channel is shown in Figure 2**a.**

The symmetric BCP-1 with PEO volume fraction (f_{PEO}) of 45% tends to form lamellar structures; however, due to the high concentration of perovskite in BCP-1/$MAPbBr_3$, PS self-organized into vertical aligned cylinders in the PEO/$MAPbBr_3$ matrix as shown in Figure 2b where the dark region corresponds to the PEO domains incorporating the $MAPbBr_3$ crystals. The highly asymmetric PS-*b*-PEO with f_{PEO} of 20% in BCP-2/$MAPbBr_3$ showed theoretical PEO/$MAPbBr_3$ sphere nanodomains with high concentration of perovskite (Figure 2c).

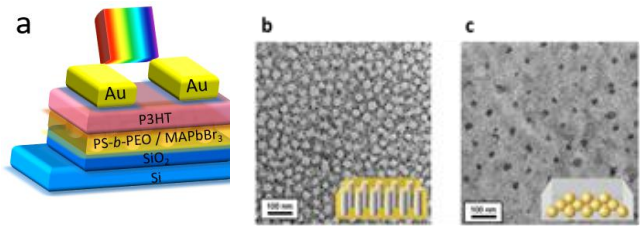

Figure 2. (a)Schematic image of the studied photomemory devices. TEM images of (b) BCP-1/$MAPbBr_3$ and (c) BCP-2/$MAPbBr_3$ composite films after annealing for 17 h in benzene vapor.

In Figure 3a and Figure 3b. Both BCP-1/$MAPbBr_3$ and BCP-2/$MAPbBr_3$ based photomemories show field-effect modulation current with ON/OFF current ratios of 4.07×10^4 and 8.15×10^3, respectively, implying the typical P3HT thin film based field-effect transistor can be successfully prepared with the anti-solvent characteristic of BCP/$MAPbBr_3$ composite film as the underlying dielectric layer. As shown in Figure 3c, the photocurrent of BCP-1/$MAPbBr_3$ system showed consistent photocurrent response in the photo-programming time ranging from 1 s to 240 s, demonstrating the rapid charge transfer rate. As the photo-programming time decreased from 1 s to 5 ms, the photocurrent is suddenly dropped to 10^{-10} A but still demonstrated a superior memory functionality even under 5 ms illumination. In striking contrast to this, in the BCP-2/$MAPbBr_3$ system (Figure 3d), the photocurrent was slightly deteriorated when the photo-programming time decreased from 240 s to 1 s. As the illumination time shifted to the range of 0.1 s to 5 ms, only temporary current response was observed. It demonstrated that the BCP-1/$MAPbBr_3$ system maintained a decent charge storage capability with an ON/OFF ratio of one order under an extremely short photo-programming time of 5 ms.

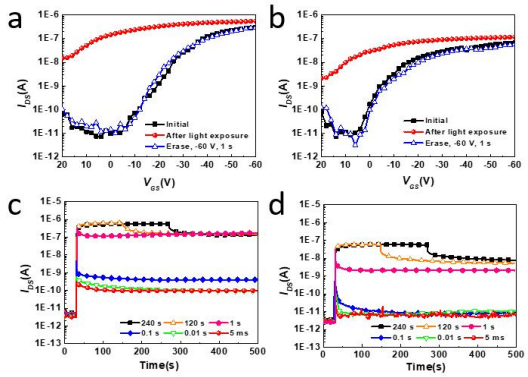

Figure 3. Photo-programming characteristics of the studied photomemory. Transfer characteristic of the perovskite-based photomemory at V_{DS} = −60 V: (a) BCP-1/$MAPbBr_3$, (b) BCP-2/$MAPbBr_3$. Temporal I_{DS} curves at V_{DS} = −60 V with different illuminating time ranging from 5 ms to 240 s: (c) BCP-1/$MAPbBr_3$, (d) BCP-2/$MAPbBr_3$.

The plausible operating mechanism of BCP/$MAPbBr_3$ based photomemory was proposed as illustrated in Figure 4a. Under blue- or green-light illumination, the photo-excited electrons and holes are generated within perovskite. Since the energy level difference between perovskite and P3HT, the holes would transfer to the P3HT and serve as charge-carriers in the active channel while the electrons would be trapped in the non-continuous perovskite phase to inhibit the trapped charge dissipation. The photo-programmed photomemory can be further erased by applying the negative gate bias to prompt the hole injection from P3HT to perovskite. Due to the morphological difference in the two varying block ratios of PS-*b*-PEO, the large interfacial area and direct contact between perovskite/PEO and P3HT in BCP-1/$MAPbBr_3$ endow the derived photomemory with higher photocurrent and faster charge transfer rate between the perovskite and the P3HT.

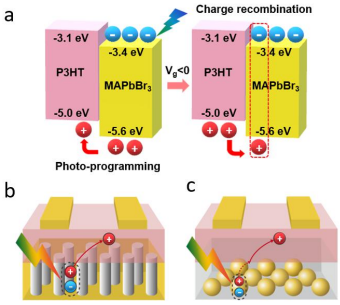

Figure 4. (a) Schematic diagram of operating mechanism under blue- and green-light illumination. Schematic diagrams of charge transfer process between BCP/$MAPbBr_3$ composite films and P3HT for (b) BCP-1/$MAPbBr_3$ and (c) BCP-2/$MAPbBr_3$ derived photomemory.

Conclusion

In summary, the spatially addressable perovskite in PS-*b*-PEO/perovskite composite film as photoactive floating gate was demonstrated to elucidate the effect of morphology on the photo-responsive characteristics of photomemory for the first time. The anti-solvent properties of PS-*b*-PEO/perovskite composite film enabled the solution-processable conjugated polymer as active channel to broaden the absorption spectrum. Through manipulating the interfacial area between perovskite and active channel in terms of the volume fraction of PS and PEO segments, ON/OFF current ratio of 10^4 and extremely low programming time of 5 ms can be achieved.

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Reference

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