Solution-processed perovskite and semiconducting carbon nanotube hybrid high-performance p-type (photo)transistors

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ABSTRACT

Although organic-inorganic halide perovskites continue to generate considerable interest with the high potential to be widely applied in a variety of optoelectronic devices, there are some critical obstacles to practical applications such as the toxicity of lead, the relatively low field effect mobility and the strong hysteresis during operation. Here we develop a universal approach to significantly improve mobility and operational stability, and reduce the hysteresis of perovskite-based transistors simultaneously through coupling low-dimensional lead-free perovskite material ($(C_6H_5C_2H_4NH_3)_2SnI_4$ (hereafter abbreviated as $(PEA)_2SnI_4$) with embedded conjugated polymers wrapped semiconducting carbon nanotubes (semi-CNTs). In the $(PEA)_2SnI_4$/semi-CNTs hybrid systems, semi-CNTs can contribute as smooth tracks for carriers to transport with less scattering and trapping of perovskite grain boundaries. We also demonstrate the extraordinary performance of $(PEA)_2SnI_4$/semi-CNTs hybrid phototransistors with ultrahigh photoresponsitivity and photosensitivity, which is found to be on a par with the best devices available to date.

1 INTRODUCTION

Organic-inorganic halide perovskite has been reported as a bright star among semiconducting materials for various optoelectronic applications, with many great examples in specific fields of solar cells, light-emitting diodes (LEDs), and photodetectors. The main advantages of this versatile and attractive material family are not only superior carrier transport inheriting from inorganic semiconductors, but also solution-processability and flexibility inheriting from organic semiconductors. Although the reports on superior optoelectronic devices using perovskite materials have increased explosively, the development of electronic devices such as thin film transistors (TFTs) is much slower, even though the first solution-processed perovskite TFT have been reported around two decades ago with a two-dimensional (2D) perovskite material, $(C_6H_5C_2H_4NH_3)_2SnI_4$ (hereafter abbreviated as $(PEA)_2SnI_4$).[1] Compared with three-dimensional (3D) counterparts (e.g. $CH_3NH_3PbI_3$), the 2D perovskites are expected to be an ideal channel materials for TFTs because the 2D layered structure have excellent compatibility with transistors that mainly use horizontal charge transport. Additionally, $(PEA)_2SnI_4$ is lead-free, meeting the imperative demand to develop lead-free perovskite materials for practical environmental friendly applications, as the toxicity issue of lead remains a thorny problem for the long run.

For the perovskite TFT development, in addition to improving mobility, reducing the anomalous current-voltage hysteresis observed at different voltage scan directions is another important and imperative challenge since most TFT applications require the identical threshold voltage during continuous operation.[2-4] It has been proposed that solution-processed pristine perovskite polycrystalline films generally suffer from some imperfections such as grain boundaries, trapping defects, and drifting ions, which are regarded as the probable origin of hysteresis.[5, 6] Recently, interfacing perovskite films with other functional materials has been suggested as an effective method to achieve optimal performance of a variety of perovskite-based optoelectronic devices due to the synergistic effect of individual building blocks.[7-10] Inspired by the outstanding physical and (opto)electrical properties of conjugated polymers wrapped semiconducting carbon nanotubes (semi-CNTs), we assumed that marrying perovskites with semi-CNTs in composite films should be a viable approach toward high-performance (opto)electronics. The grain boundaries that are known for the enrichment regions of charge traps, can be reduced across the high-way-like carrier transport path, which is the role that semi-CNTs play in the hybrid films.[11]

In this work, we report hybrid materials based on coupling lead-free perovskite with embedded conjugated polymers (poly(9,9-di-n-dodecylfluorene), PFDD) wrapped semi-CNTs for high-performance and stable solution-processable TFTs and phototransistors. With the addition of semi-CNTs in $(PEA)_2SnI_4$ films, the TFT mobility, hysteresis and stability as well as photodetectivity are dramatically improved through the reduction of scattering and trapping effects at grain boundaries of polycrystalline $(PEA)_2SnI_4$ films.

2 EXPERIMENT

Perovskite/semi-CNTs precursor preparation:

Purchased PEAI (Xi'an Polymer Light Technology Corp.) and SnI_2 (Alfa Aesar) were dissolved in DMF at a stoichiometric molar ratio of 2:1 and kept at 60 °C for 2h in a glove box. For $(PEA)_2SnI_4$/semi-CNTs mixture precursor, desired amount of semi-CNTs suspension (5, 10, and 20 vol. %) were added into 0.5 mL pure $(PEA)_2SnI_4$ solution in glove box. Details of semi-CNTs suspension preparation can be found in our previous reports.[12] The mixture suspensions were bath-sonicated for 30 min prior to spun on SiO_2/Si substrates at 4000 rpm for 30 s. The 40-nm Au source and drain electrodes were deposited by thermal evaporation using a shadow mask.

3 RESULTS and DISCUSSION

3.1. Solution-processed $(PEA)_2SnI_4$/semi-CNTs hybrid TFTs

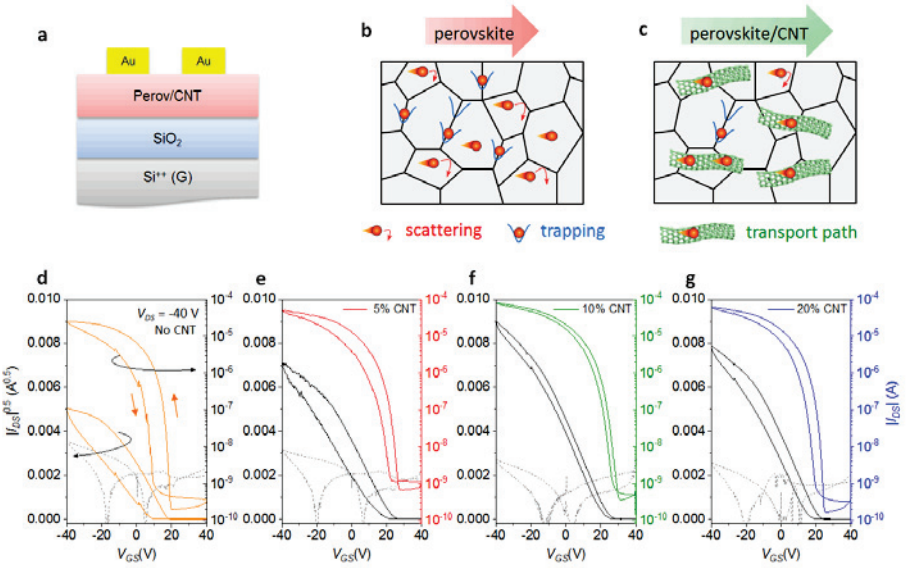

Fig. 1. (a) A TFT structure with $(PEA)_2SnI_4$/semi-CNTs hybrid films as the semiconducting layer. (b, c) Schematic illustration of the scattering and trapping by grain boundaries in pure perovskite films, and the mechanism of fast carrier transport path construction in perovskite/semi-CNTs hybrid systems. (d-g) Transfer characteristics of pure and hybrid TFTs with different amount of semi-CNTs.

We designed $(PEA)_2SnI_4$/semi-CNTs hybrid transistors (Fig. 1a). As schematically shown in Fig. 1b and 1c, the carrier scattering and trapping related to grain boundaries, which are known for the enrichment regions of charge traps, can be subdued in $(PEA)_2SnI_4$/semi-CNTs hybrid systems, where semi-CNTs can act as the high-way-like carrier transport path. Correspondingly, compared with pure $(PEA)_2SnI_4$ transistors (Fig. 1d), the $(PEA)_2SnI_4$/semi-CNTs hybrid ones with 5% of semi-CNTs exhibited improved mobility to 0.82 ± 0.17 cm^2/Vs, as well as reduced dual-sweep hysteresis from 14.5 V to 9.6 V (Fig. 1e). For the $(PEA)_2SnI_4$/semi-CNTs hybrid transistors with 10% of semi-CNTs, device mobility increased by around threefold to 1.51 ± 0.15 cm^2/Vs with impressively decreased ΔV_H of 1.1 V (Fig. 1f). When the ratio of the semi-CNTs increases up to 20%, the performance of composite TFTs was rather reduced by mobility of 1.05 ± 0.20 cm^2/Vs and ΔV_H of 6.4 V (Fig. 1g). This is probably due to the increased disordering effect by adding an excess of semi-CNTs over the optimal amount.

In addition to promising electrical properties, $(PEA)_2SnI_4$/semi-CNTs film also showed intensive photoresponse for a broad spectrum range from visible to near infrared region (Fig. 2a and 2b). To explore the optoelectrical synergistic effect of perovskite and semi-CNTs, we investigated the performance of pure $(PEA)_2SnI_4$ and $(PEA)_2SnI_4$/10% semi-CNTs hybrid devices working as three-terminal phototransistors, which possess superior sensitivity to two-terminal photodetectors, such as the abilities to reduce noise and amplify electrical signals, and are welcomely target for image sensing, optical communication, environmental monitoring and chemical/biological detection.[13, 14] Fig. 2c and 2d show the transfer characteristics of $(PEA)_2SnI_4$ phototransistors without and with 10% semi-CNTs TFTs in dark and under light irradiation (532 nm, 3 μW/cm^2). Under illumination, both devices presented higher drain current than each in dark, and $(PEA)_2SnI_4$/10% semi-CNTs phototransistors exhibited even higher photocurrent than that of pure $(PEA)_2SnI_4$ ones.

The light responsive properties of the optoelectronic devices are generally quantified by determining the photoresponsivity (R) and the photoswitching ratio, i.e., photosensitivity (P) (photocurrent/dark-current), which has been accomplished by measuring the I-V characteristics of the transistors under white or monochromatic light illumination. The R and P values are defined as

$$R = \frac{(I_{light} - I_{dark})}{EWL}$$

$$P = \frac{(I_{light} - I_{dark})}{I_{dark}}$$

where I_{light} and I_{dark} are the drain current under light irradiation and in dark state, E is the incident illumination power density, and W and L are the channel width and length.[15] The R and P values are plotted as a function of V_{GS} for phototransistors. As shown in Fig. 2e and 2f, the R and P values of pristine $(PEA)_2SnI_4$ phototransistors were found to be 8.3×10^3 A/W and 7.2×10^4, while the

values of $(PEA)_2SnI_4$/10% semi-CNTs hybrid devices reached 6.3×10^4 A/W and 4.7×10^5, respectively. Such performance is among the best solution-processed perovskite-based phototransistors ever reported. The conventional single-crystal Si phototransistor exhibited the *R* value of 300 A/W, which is regarded as the assessment reference of a photodetector.[16, 17] Besides *R* and *P*, the wavelength-dependent gain was calculated to be as high as 1.5×10^5 by the formula $\text{Gain}_{\square} = R_\lambda \times E_{hv}$, where R_λ is photoresponsivity corresponding to incident light wavelength, and E_{hv} is the energy of the incident photon (in eV).[18] Additionally, both the pure and hybrid phototransistors exhibited clear dynamic response under modulated irradiation (Fig. 2g and 2h), illustrating that light acts as additional gate to modulate the drain current of transistors.

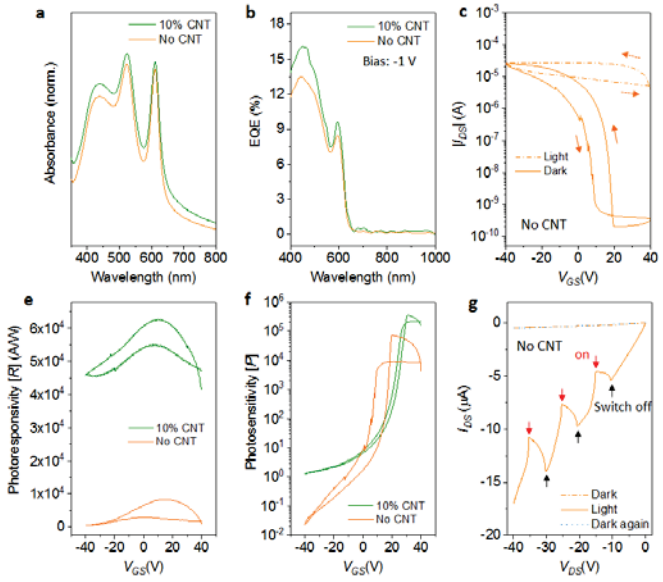

Fig. 2 (a) Absorbance and (b) external quantum efficiency (EQE) spectra of $(PEA)_2SnI_4$ films without and with 10% semi-CNTs. (c, d) Transfer curves of $(PEA)_2SnI_4$ without and with 10% semi-CNTs devices in dark and under light irradiation (532 nm, 3 μW/cm^2). (e, f) Photoresponsivity (*R*) and photosensitivity (*P*) versus V_{GS} of the devices under light irradiation. Output characteristics of perovskite phototransistors (g) without and (h) with 10% semi-CNTs measured in the dark or under light irradiation (V_{GS} = 15 V). The light was switched on and off manually during the measurement.

4 CONCLUSIONS

We have reported the first processing of 2D layered perovskite materials $(PEA)_2SnI_4$ and conjugated polymers wrapped semi-CNTs hybrid transistors. Compared to the pure $(PEA)_2SnI_4$ counterparts, the hybrid films with semi-CNTs as smooth carrier transport tracks showed greatly reduced dual-sweep hysteresis, improved field-effect mobility, and higher operation stability in TFTs by grain boundary engineering. Moreover, we have demonstrated the photodetecting properties of $(PEA)_2SnI_4$/semi-CNTs hybrid phototransistors with extraordinarily high photoresponsivity, photosensitivity, and gain. This universal strategy demonstration of low-dimensionality Sn(II) perovskites and semi-CNTs hybrid systems offers promising prospects for the development of high-performance lead-free perovskite/nanomaterials-based optoelectronics.

5 ACKNOWLEDGEMENTS

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REFERENCES

[1] Kagan, C.; Mitzi, D.; Dimitrakopoulos, C., Organic-inorganic hybrid materials as semiconducting channels in thin-film field-effect transistors. *Science,* Vol.286, pp. 945 (1999).

[2] Chin, X. Y.; Cortecchia, D.; Yin, J.; Bruno, A.; Soci, C., Lead iodide perovskite light-emitting field-effect transistor. *Nat. Commun.,* Vol.6, pp. 7383 (2015).

[3] Labram, J. G.; Fabini, D. H.; Perry, E. E.; Lehner, A. J.; Wang, H.; Glaudell, A. M.; Wu, G.; Evans, H.; Buck, D.; Cotta, R., Temperature-dependent polarization in field-effect transport and photovoltaic measurements of methylammonium lead iodide. *J. Phys. Chem. Lett.,* Vol.6, pp. 3565 (2015).

[4] Senanayak, S. P.; Yang, B.; Thomas, T. H.; Giesbrecht, N.; Huang, W.; Gann, E.; Nair, B.; Goedel, K.; Guha, S.; Moya, X., Understanding charge transport in lead iodide perovskite thin-film field-effect transistors. *Sci. Adv.,* Vol.3, pp. e1601935 (2017).

[5] Jie, C.; Xia, T. S.; A., B. P.; Ching-Ping, W.; Ni, Z., Interstitial Occupancy by Extrinsic Alkali Cations in Perovskites and Its Impact on Ion Migration. *Adv. Mater.,* Vol.30, pp. 1707350 (2018).

[6] Son, D.-Y.; Kim, S.-G.; Seo, J.-Y.; Lee, S.-H.; Shin, H.; Lee, D.; Park, N.-G., Universal Approach toward Hysteresis-Free Perovskite Solar Cell via Defect Engineering. *J. Am. Chem. Soc.,* Vol.140, pp. 1358 (2018).

[7] Li, F.; Wang, H.; Kufer, D.; Liang, L.; Yu, W.; Alarousu, E.; Ma, C.; Li, Y.; Liu, Z.; Liu, C., Ultrahigh Carrier Mobility Achieved in Photoresponsive Hybrid Perovskite Films via Coupling with Single‐Walled Carbon Nanotubes. *Adv. Mater.,* Vol.29, pp. 1602432 (2017).

[8] Roy, K.; Padmanabhan, M.; Goswami, S.; Sai, T.

P.; Ramalingam, G.; Raghavan, S.; Ghosh, A., Graphene–MoS2 hybrid structures for multifunctional photoresponsive memory devices. *Nat. Nanotechnol.,* Vol.8, pp. 826 (2013).
[9] Shao, Y.; Liu, Y.; Chen, X.; Chen, C.; Sarpkaya, I.; Chen, Z.; Fang, Y.; Kong, J.; Watanabe, K.; Taniguchi, T.; Taylor, A.; Huang, J.; Xia, F., Stable Graphene-Two-Dimensional Multiphase Perovskite Heterostructure Phototransistors with High Gain. *Nano Lett.,* Vol.17, pp. 7330 (2017).
[10] Matsushima, T.; Hwang, S.; Sandanayaka, A. S.; Qin, C.; Terakawa, S.; Fujihara, T.; Yahiro, M.; Adachi, C., Solution‐Processed Organic–Inorganic Perovskite Field‐Effect Transistors with High Hole Mobilities. *Adv. Mater.,* Vol.28, pp. 10275 (2016).
[11] Li, X.; Yu, D.; Chen, J.; Wang, Y.; Cao, F.; Wei, Y.; Wu, Y.; Wang, L.; Zhu, Y.; Sun, Z., Constructing fast carrier tracks into flexible perovskite photodetectors to greatly improve responsivity. *ACS Nano,* Vol.11, pp. 2015 (2017).
[12] Ji, D.; Lee, S.-H.; Noh, Y.-Y., Selective dispersion of high-purity semiconducting carbon nanotubes using indacenodithiophene-based conjugated polymer. *Appl. Phys. Lett.,* Vol.112, pp. 033103 (2018).
[13] Wang, H.; Kim, D. H., Perovskite-based photodetectors: materials and devices. *Chem. Soc. Rev.,* Vol.46, pp. 5204 (2017).
[14] Kang-Jun, B.; Maddalena, B.; Dario, N.; Mario, C.; Yong-Young, N., Organic Light Detectors: Photodiodes and Phototransistors. *Adv. Mater.,* Vol.25, pp. 4267 (2013).
[15] Rekab, W.; Stoeckel, M.-A.; El Gemayel, M.; Gobbi, M.; Orgiu, E.; Samorì, P., High-Performance Phototransistors Based on PDIF-CN2 Solution-Processed Single Fiber and Multifiber Assembly. *ACS Appl. Mater. Interfaces,* Vol.8, pp. 9829 (2016).
[16] Johnson, N. M.; Chiang, A., Highly photosensitive transistors in single‐crystal silicon thin films on fused silica. *Appl. Phys. Lett.,* Vol.45, pp. 1102 (1984).
[17] Yutaka, W.; Ryoma, H.; Hoon-Seok, S., Recent progress in photoactive organic field-effect transistors. *Sci. Technol. Adv. Mater.,* Vol.15, pp. 024202 (2014).
[18] Dong, R.; Fang, Y.; Chae, J.; Dai, J.; Xiao, Z.; Dong, Q.; Yuan, Y.; Centrone, A.; Zeng, X. C.; Huang, J., High‐Gain and Low‐Driving‐Voltage Photodetectors Based on Organolead Triiodide Perovskites. *Adv. Mater.,* Vol.27, pp. 1912 (2015).