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# Advances in lead-free perovskite phototransistors

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**Abstract**

Perovskites have been a popular research focus in the solar cell industry for the previous two decades for its high efficiency and low cost. Recently, the interest in perovskites have expanded into other electrical devices that include phototransistors. With increasing environmental concern regarding perovskite toxicity, lead-free perovskites have become a large focus in research. This review highlights recent research of different lead-free perovskites and gives insight into their effectiveness as phototransistors

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## 1. Introduction

A phototransistor is an electronic component that relies on light exposure to switch and amplify current. Phototransistors have a three-terminal configuration that consists of a conductive channel source, drain electrodes, and gate terminal [1]. Current is able to flow when light photons hit the semiconducting material of the photoactive medium which allows for electrons to move. The current is controlled by the gate terminal depending on the intensity of the light.

Perovskites are materials that have the chemical formula of $ABX_3$ and the same crystal structure as calcium titanium oxide. Perovskites have long been popular in perovskite solar cells (PSCs) in which the sunlight-to-electrical-power conversion efficiency of 29.1% beats the 27% record of conventional silicon cells [2]. It is only recently that perovskites are being researched for use in other devices such as phototransistors as the light absorber. Perovskites have gained attention for LEDs, lasers, and photodetectors due to their high carrier mobility, high optical absorption, long carrier diffusion lengths, and cheap and easy fabrication processes. Despite these advantages, perovskites often contain lead which is toxic to living organisms and can contaminate the environment [3]. As a result, it is important to develop environmentally friendly alternatives. This review discusses several recent lead-free perovskite materials and their performance as phototransistors.

## 2. Layer-by-layer inorganic lead-free bismuth perovskite and SWCNTs

Sn and Ge elements have long been considered for the use in lead-free perovskites, but they readily oxidize in the air, resulting in poor stability [4]. On the other hand, Bi-based perovskite have long-term stability and photosensitivity, but low charge conductivity. The alternative would be to integrate the perovskite with other materials. Although graphene and single-walled carbon nanotubes (SWCNTs) both have high photoresponsivity, graphene lacks a band gap and have a low light to dark intensity ratio. SWCNTs have both high mobility and reduced off-current which makes it the ideal material to be used with bismuth perovskite [5].

Liu et al. synthesized a layer-by-layer structure by sequential spin-coating of SWCNTs and $CsBi_3I_{10}$ suspensions followed by thermal annealing. From the photoluminescence (PL) spectra of the pure $CsBi_3I_{10}$ film and $CsBi_3I_{10}$/SWCNTs film, this shows that while both films peaked at 750 nm, the recombination of the photogenerated carriers was suppressed for the hybrid film [6]. This is supported by the results in the transient absorption spectra, showing a decrease in the lifetime of photogenerated carriers for the hybrid film [6]. This means that there is more rapid hole extraction and fast photogenerated carriers' lifetimes and thus higher performance. The researchers also considered the photoresponsivity (R, the photoelectric conversion), photo-detectivity (D*, affect by dark current), and the photon to electron conversion efficiency (EQE).

Liu et al. were able to find that the $CsBi_3I_{10}$/SWCNTs film had a photoresponsivity of 6.0 * $10^4$ $AW^{-1}$, photo-detectivity of 2.46 * $10^{14}$ jones, and EQE of 1.66 * $10^5$ %. In comparison, pure $CsBi_3I_{10}$ had a photoresponsivity of 21.8 $AW^{-1}$, photo-detectivity of 1.93 * $10^{13}$ jones, and EQE of 4.13 * $10^3$ % [6]. The light and dark intensity at 45-60% relative humidity was examined for the 500 hours test showing little to no degradation, indicating long-term stability [6]. Liu et al. also found that the device could demonstrate short-term synaptic behaviors such as excitatory postsynaptic current (EPSC) and paired pulse facilitation (PPF) that could be controlled by light pulse width and intensity.

These results demonstrate that lead-free $CsBi_3I_{10}$/SWCNTs hybrid phototransistors are possible and can have excellent photodetection and synaptic performance. This sets a foundation for further research into hybrid lead-free phototransistors that can also be applied in biomedical research.

## 3. $(PEA)_2SnI_4$ and semi-CNT wrapped conjugated polymer

Although $(C_6H_5C_2H_4NH_3)_2SnI_4$, also known as $(PEA)_2SNI_4$, has been used in solution processed perovskite thin film transistors for the past two decades, obstacles such as low field effect mobility and hysteresis still exist that negatively impacts the operational stability [7]. The hysteretic behavior can be reduced by combining the perovskite films with a material that would allow for a reduction in the carrier trapping by defects. One material that stands out is the conjugated polymer (poly (9,9-di-n-dodecylfluorene, PFDD) wrapped semiconducting carbon nanotubes (semi-CNTs) which has carrier transport tracks that could help reduce the carrier trapping by defects.

Zhu et al. synthesized the substrates by sequential spin-coating of a $(PEA)_2SNI_4$/semi-CNT precursor suspension followed by thermal annealing [8]. In evaluating the photodetection of the $(PEA)_2SNI_4$/semi-CNT hybrid phototransistor, the R was found to be 6.3*$10^4$ $AW^{-1}$ and the D* was 1.12 * $10^{17}$ jones, which are the record values for perovskite-based phototransistors at the time of writing. This high detection is possible as the result of suppressed carrier trapping by the hybrid structure. These results indicate the capability of using Sn perovskites in semi-CNT hybrid systems and the promising prospects it has on other optoelectronics in addition to phototransistors.

## 4. Solution-processed double perovskite $Cs_2AgBiBr_6$ films

While $ABX_3$ is the more common formula for perovskites, an alternative $A_2BBX_6$ double perovskite structure has attracted increasing attention. The most promising lead-free perovskite of this form is $Cs_2AgBiBr_6$. It has been found that for $Cs_2AgBiBr_6$ single crystals in solar cells, there is high defect tolerance, material stability, and long carrier recombination lifetime [9].

Li et al. created the $Cs_2AgBiBr_6$ films by spin-coating the precursor solution on top of a n-GaN/Al2O2 substrate and annealing [10]. Because of $Cs_2AgBiBr_6$'s efficient interfacial charge transfer effect, the photodetectors were found to have an on/off ratio of 4.16 *$10^4$, R of 1.46 $AW^{-1}$ and D* of 0.94 * $10^{13}$ jones [10]. Additionally, these devices were stable against both water and oxygen degradation at air ambient and 35-50% humidity. Even when tested at higher working temperatures of 373 K for 10 hours continuously and in the air for a 3-month storage, it was found that the photodetection ability was maintained. This indicates that the device has good temperature resistance even under harsh conditions. Li et al. also experimented with using the photodetector as the sensing pixels in an imaging system. This resulted in a high-resolution imaging pattern [10].

These results indicate that $Cs_2AgBiBr_6$ is not only a good candidate for highly efficient and stable photodetectors but also in optical imaging. This sets an example for a functional alternative perovskite structure and gives room for more research in this area.

## 5. Conclusions

Traditional perovskite phototransistors have higher mobility and stability compared to lead-free perovskite phototransistors but are toxic to the environment. For this reason, there has been a great need for the development of modifications to improve lead-free perovskite performance. In this review, three recently developed lead-free perovskite modifications were introduced; $CsBi_3I_{10}$/SWCNTs, $(PEA)_2SNI_4$/semi-CNT, and $Cs_2AgBiBr_6$. These new developments have shown remarkable improvements in the areas of responsivity and photo-detectivity, with $(PEA)_2SNI_4$/semi-CNT holding the record for perovskite-based phototransistors. In addition to use in optoelectronics, other applications found include analyzing short term synaptic behavior and optical imaging. Some possible areas of research include alternative perovskite structures and hybrid perovskites. With continued advancements in lead-free perovskite phototransistors, this can lead to their application in many other fields, including medical devices, tissue engineering, and cell growth regulation.

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## Conflict of Interest

The author has no conflict of interest.

## References

[1] K.-J. Baeg, M. Binda, D. Natali, M. Caironi, and Y.-Y. Noh, "Organic Light Detectors: Photodiodes and Phototransistors," *Advanced Materials*, vol. 25, no. 31, pp. 4267–4295, 2013. doi:10.1002/adma.201204979.

[2] Wu, Thakur, Chiang, Chandel, Wang, Chiu, and Chang, “The Way to Pursue Truly High-Performance Perovskite Solar Cells,” *Nanomaterials*, vol. 9, no. 9, p. 1269, 2019. doi:10.3390/nano9091269.

[3] W. Ke and M. G. Kanatzidis, “Prospects for low-toxicity lead-free perovskite solar cells,” *Nature Communications*, vol. 10, no. 1, 2019. doi:10.1038/s41467-019-08918-3.

[4] T. Krishnamoorthy, H. Ding, C. Yan, W. L. Leong, T. Baikie, Z. Zhang, M. Sherburne, S. Li, M. Asta, N. Mathews, and S. G. Mhaisalkar, “Lead-free germanium iodide perovskite materials for photovoltaic applications,” *Journal of Materials Chemistry A*, vol. 3, no. 47, pp. 23829–23832, 2015. doi:10.1039/c5ta05741h.

[5] Y. Lee, J. Kwon, E. Hwang, C.-H. Ra, W. J. Yoo, J.-H. Ahn, J. H. Park, and J. H. Cho, “High-Performance Perovskite-Graphene Hybrid Photodetector,” *Advanced Materials*, vol. 27, no. 1, pp. 41–46, 2014. doi:10.1002/adma.201402271.

[6] Z. Liu, S. Dai, Y. Wang, B. Yang, D. Hao, D. Liu, Y. Zhao, L. Fang, Q. Ou, S. Jin, J. Zhao, and J. Huang, “Photoresponsive Transistors Based on Lead-Free Perovskite and Carbon Nanotubes,” *Advanced Functional Materials*, vol. 30, no. 3, p. 1906335, 2019. doi:10.1002/adfm.201906335.

[7] X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, and C. Soci, “Lead iodide perovskite light-emitting field-effect transistor,” *Nature Communications*, vol. 6, no. 1, 2015. doi:10.1038/ncomms8383.

[8] H. Zhu, A. Liu, H. L. Luque, H. Sun, D. Ji, and Y.-Y. Noh, “Perovskite and Conjugated Polymer Wrapped Semiconducting Carbon Nanotube Hybrid Films for High-Performance Transistors and Phototransistors,” *ACS Nano*, vol. 13, no. 4, pp. 3971–3981, 2019. doi:10.1021/acsnano.8b07567.

[9] Z. Shi, S. Li, Y. Li, H. Ji, X. Li, D. Wu, T. Xu, Y. Chen, Y. Tian, Y. Zhang, C. Shan, and G. Du, “Strategy of Solution-Processed All-Inorganic Heterostructure for Humidity/Temperature-Stable Perovskite Quantum Dot Light-Emitting Diodes,” *ACS Nano*, vol. 12, no. 2, pp. 1462–1472, 2018. doi:10.1021/acsnano.7b07856.

[10] Y. Li, Z. Shi, L. Lei, S. Li, D. Yang, D. Wu, T. Xu, Y. Tian, Y. Lu, Y. Wang, L. Zhang, X. Li, Y. Zhang, G. Du, and C. Shan, “Ultrastable Lead-Free Double Perovskite Photodetectors with Imaging Capability,” *Advanced Materials Interfaces*, vol. 6, no. 10, p. 1900188, 2019. doi:10.1002/admi.201900188.