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Perspective

# Rise of ecofriendly $AgBiS_2$ nanocrystal solar cells

Junwei Liu [a,b,c], Jingjing Wang [a,c], Wenchao Zhao [d], Zhihua Zhou [b,*], Long Ye [a,c,e,*]

[a] School of Materials Science and Engineering, Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300350, China
[b] School of Environmental Science and Engineering, Tianjin University, Tianjin 300350, China
[c] State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130000, China
[d] Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China
[e] Hubei Longzhong Laboratory, Xiangyang 441000, China

During the past decade, nanocrystal solar cells have attracted worldwide research attention due to their high absorption coefficient, broad and tunable absorption range, and promising multiple exciton generation. With joint efforts, great performance breakthroughs have been achieved in the field of nanocrystal solar cell technology, with a certified efficiency of 18.1% for perovskite nanocrystal solar cells (https://www.nrel.gov/pv/cell-efficiency.html) and a record efficiency of 15.4% for PbS nanocrystal solar cells [1]. Despite the striking advances, the high toxicity of Pb-based nanocrystal materials raises great concerns when introduced into consumer electronics. Environmental concerns have opened an opportunity for the exploration of ecofriendly alternatives.

Abundant research efforts are encouraged to develop non-toxic nanocrystal materials for high-performance solar cells. The well-developed I–III–VI group nanocrystals, e.g., Zn–Cu–In–Se or Zn–Cu–In–S nanocrystals, have enabled the significant advancement of dye-sensitized solar cells [2,3]. In particular, continuous efforts by Zhong's group [4,5] have enhanced the photovoltaic performance of nanocrystal-sensitized solar cells to ~15.3%. For solar cells with a planar heterojunction, ecofriendly and earth-abundant $AgBiS_2$ nanocrystals emerge as promising candidates due to their favorable energy levels and ultra-high absorption coefficients. For instance, $AgBiS_2$ nanocrystals have suitable conduction and valence bands, which can form an excellent energy level alignment with electron and hole transport materials, thereby enabling great photovoltaic performance. Moreover, $AgBiS_2$ nanocrystals exhibit a broad absorption range to ~1200 nm with an exceedingly high absorption coefficient approaching $10^6$ $cm^{-1}$, which is 5–10 times greater than those of other photovoltaic materials [6]. Therefore, ultrathin solar cells, i.e., ~30 nm, can deliver a high short-circuit current density ($J_{sc}$) over 25 mA/$cm^2$ [6]. In addition, ultrathin $AgBiS_2$ nanocrystal solar cells can not only significantly reduce material consumption but also facilitate carrier collection, which can deliver high photovoltaic performance. Moreover, $AgBiS_2$ solar cells hold great application potential in flexible and lightweight electronic devices.

In 2013, $AgBiS_2$ nanocrystals were employed in sensitized solar cells, delivering a low power conversion efficiency (PCE) of ~0.53% [7]. The first breakthrough of $AgBiS_2$ nanocrystal solar cells emerged in 2016. In the study, Konstantatos's group [8] demonstrated that p–i–n heterojunction can markedly enhance the PCE to ~6.3% with no hysteresis. Moreover, ecofriendly solar cells can achieve a high $J_{sc}$ of ~22 mA/$cm^2$ with an extremely thin photoactive layer of ~35 nm, revealing the great application potential in ultralight and ultrathin solar cells. Nevertheless, nearly no progress was made in the following five years for this non-toxic nanocrystal solar cell.

Until recently, $AgBiS_2$ nanocrystal solar cells have witnessed a striking rise with a new breakthrough in their performance and stability. Konstantatos's group [6] further enhanced the PCE of the ecofriendly solar cells from ~6.0% to over 9.0% with markedly improved operation stability under ambient conditions. The great advancement was mainly attributed to the following reasons. First, the absorption coefficient was enhanced via engineering cation disorder. They developed a low-temperature and scalable annealing strategy, which can engineer the cations of $AgBiS_2$ nanocrystals, resulting in an extremely high absorption coefficient (5–10 times greater than that of any other photovoltaic materials). Second, organic ligands were used for $AgBiS_2$ nanocrystal passivation. They employed 3-mercaptopropionic acid for nanocrystal passivation, outperforming that with tetramethylammonium iodide and ethane-dithiol, which have been widely used in well-developed PbS nanocrystals. Third, poly(triarylamine) (PTAA) was employed as the hole transport layer (HTL). The work claimed that a uniform PTAA can reduce interface recombination and suppress current leakage, resulting in significantly enhanced photovoltaic performance over that with the previously used PTB7 (9.17% vs. 7.63%). With these benefits, the developed $AgBiS_2$ nanocrystal solar cells can deliver a record PCE of 9.17% and retain ~80% of the initial performance after 40 h in ambient conditions. The work has reactivated the research of ecofriendly $AgBiS_2$ nanocrystal solar cells. Nevertheless, the photovoltaic performance of $AgBiS_2$ nanocrystals still lags far behind those of PbS and perovskite nanocrystal counterparts (over 15%). Hence, more efforts are needed to make further performance breakthroughs for ecofriendly $AgBiS_2$ nanocrystal

* Corresponding authors.
*E-mail addresses:* zhuazhou@tju.edu.cn (Z. Zhou), yelong@tju.edu.cn (L. Ye).

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solar cells, and promising research directions are provided as follows.

*Enhancing nanocrystal passivation.* To date, $AgBiS_2$ nanocrystal solar cells still suffer from severe energy loss, even over half of the bandgap (~1.1 eV), significantly higher than those of PbS nanocrystal (~0.45 eV) and perovskite nanocrystal solar cells (~0.35 eV) [9]. The great energy loss mainly stems from the high-density trap and energy disorder, which can be clearly observed from external quantum efficiency (EQE) results (Fig. 1a, b). The shallow absorption edge of $AgBiS_2$ nanocrystals placed great restrictions on the further photocurrent improvement of solar cells [10]. To address this tough challenge, it is highly desirable to devote more efforts to identifying the true defect density of $AgBiS_2$ nanocrystals through various characterizations. Subsequently, more passivation strategies are encouraged to be developed to reduce the pernicious trap density and enhance the mobility of $AgBiS_2$ nanocrystals. A similar lattice structure with PbS nanocrystals endows the great superiority of $AgBiS_2$ nanocrystals in terms of shareable passivation strategies. For instance, the widely used $AgBiS_2$ nanocrystals with TMAI passivation generally suffer from high trap-assisted carrier recombination. Kim et al. [11] recently enhanced the passivation of $AgBiS_2$ nanocrystals by introducing the further treatment with 2-mercaptoethanol ligand, which can not only reduce the trap density but also match the energy level with organic HTLs for favorable carrier transport. Nevertheless, the low open-circuit voltage ($V_{oc}$) still placed great restrictions on the performance improvement of $AgBiS_2$ nanocrystals. Hence, the high energy loss may be the main bottleneck for the further advancement of these nanocrystal solar cells. The promising routes may be inspired by the well-developed PbS nanocrystal counterparts. The success of matrix engineering for PbS nanocrystals may offer feasible solutions for better passivation, e.g., lead-free perovskite matrix.

*Simplifying film processing.* For photovoltaic applications, the long-chain ligands of $AgBiS_2$ nanocrystals should be replaced with short-chain ligands for efficient carrier hopping. The commonly used solid-state ligand exchange has enabled the great advancement of $AgBiS_2$ nanocrystal solar cells. Nevertheless, the cumbersome film processing places great restrictions on commercial applications. Hence, there is an urgent demand for developing facile processing approaches for further performance improvement and actual applications. The solution-phase ligand exchange has earned great success in PbS nanocrystals, triggering a great breakthrough in photovoltaic performance and stability. Bae et al. [13] recently developed the solution-phase ligand exchange with AgI and $BiI_3$ halometallates for $AgBiS_2$ nanocrystals. They reported that AgI-based ligands can deliver one-step film deposition, high-degree ligand exchange, sharp band tail, and low trap density, resulting in a record $V_{oc}$ of 0.55 V for $AgBiS_2$ nanocrystal solar cells. Nevertheless, the developed solar cells can only achieve an inferior $J_{sc}$ of ~12.4 mA/cm$^2$, significantly lower than that with a solid-state ligand exchange. The recent work by Konstantatos's group [14] developed promising $AgBiS_2$ nanocrystal inks with a green solvent, which can enable truly environment-friendly device processing. Moreover, the developed $AgBiS_2$ nanocrystal solar cells can deliver a high $J_{sc}$ of ~25 mA/cm$^2$. Nevertheless, solution-phase ligand

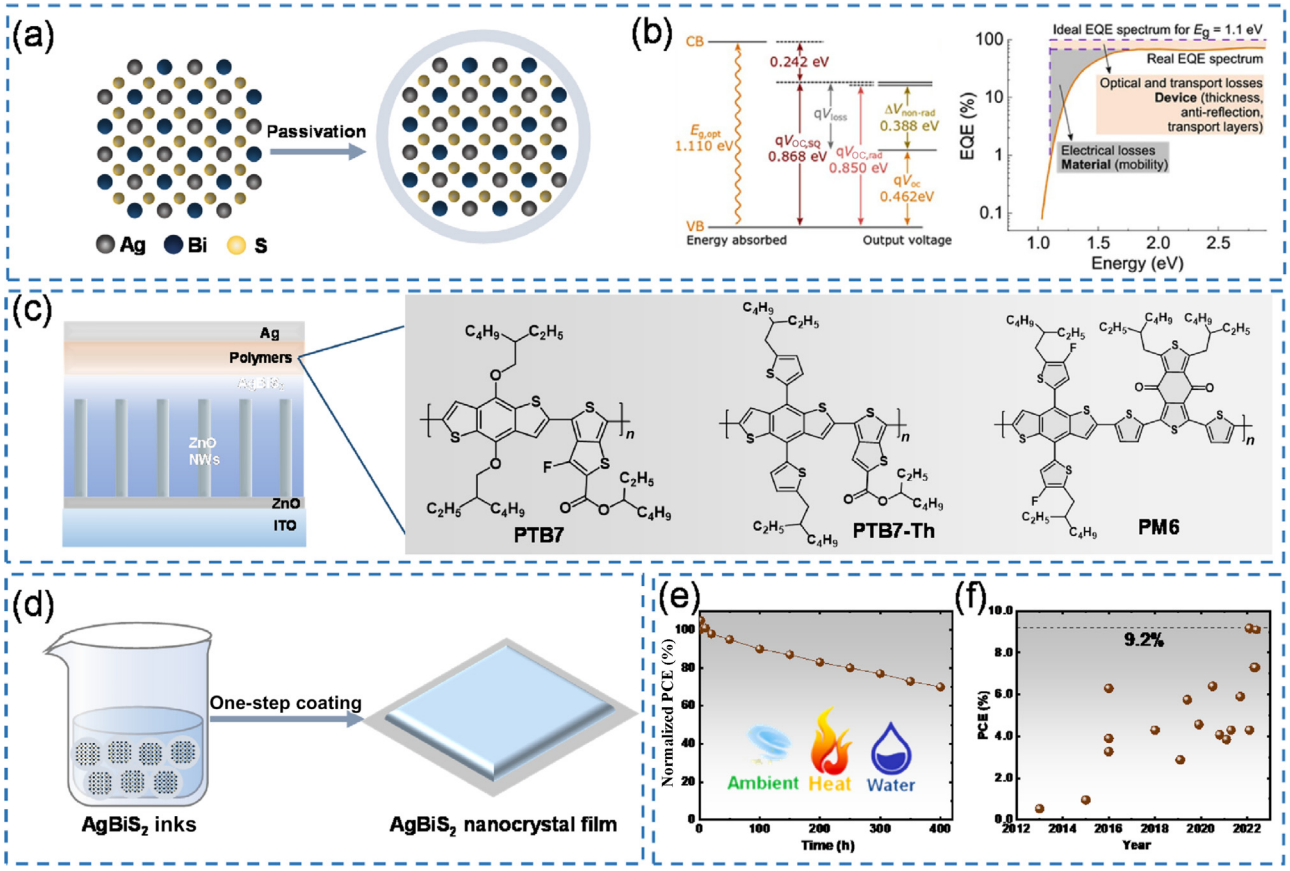


**Fig. 1.** (Color online) Promising research directions for emerging $AgBiS_2$ nanocrystals. (a) Schematic of nanocrystal passivation. (b) Schematic of the energy loss of $AgBiS_2$ nanocrystal solar cells (left panel) and the external quantum efficiency (EQE) spectra of $AgBiS_2$ nanocrystal solar cells (right panel). Reproduced with permission from Ref. [10]. Copyright © 2020 Elsevier. (c) Schematic of the device structure based on a bulk heterojunction (left panel). Molecular structure of promising organic HTLs for $AgBiS_2$ nanocrystal solar cells (right panel). (d) Schematic of film processing based on $AgBiS_2$ nanocrystal inks. (e) Stability of $AgBiS_2$ nanocrystal solar cells. Reproduced with permission from Ref. [12]. Copyright © 2021 Elsevier. (f) Progress of $AgBiS_2$ nanocrystal solar cells.

exchange still employs the hot-injection nanocrystal synthesis, which involves a high-temperature process and complicated post-treatment. Therefore, more efforts should be devoted to developing one-step film processing (Fig. 1d), which has successfully been employed in PbS nanocrystal solar cells for high performance and stability [15,16]. Konstantatos's group [17] recently designed a low-cost and room-temperature synthesis of $AgBiS_2$ nanocrystals, which can significantly reduce the production cost by 60% compared with hot-injection synthesis. However, the processing of $AgBiS_2$ solar cells still employed the prior solid-state ligand exchange, and more research efforts should be devoted to further developing the facile processing methods.

*Optimizing device structure.* The device structure also plays a critical role in the further performance breakthrough of $AgBiS_2$ nanocrystal solar cells (Fig. 1c). Bulk heterojunctions have been widely used in emerging solar cells for high-efficiency carrier extraction. Xiao et al. [18] recently investigated the performance of $AgBiS_2$ nanocrystal solar cells with ZnO nanowires, resulting in an efficient carrier extraction and high EQE from visible to near-infrared bands. In addition, organic HTLs have a great impact on the photovoltaic performance of $AgBiS_2$ nanocrystal solar cells. The previously used PTB7 and PTB7-Th presented a limited carrier extraction of $AgBiS_2$ nanocrystals, especially in near-infrared bands. Wang et al. [6] recently demonstrated that PTAA can reduce interface recombination and enhance the carrier transport from nanocrystals to organics, markedly advancing the performance of $AgBiS_2$ nanocrystal solar cells. Moreover, Kim et al. [11] reported that PM6 can form a good energy level match with $AgBiS_2$ nanocrystals, simultaneously enhancing carrier extraction and reducing energy loss. The introduction of non-fullerene acceptors into PM6 HTLs can further elevate the performance of $AgBiS_2$ nanocrystal solar cells ($J_{sc}$ from ~22 to 25 mA/cm$^2$). We deem that the existing organic HTLs cannot still arouse the photovoltaic potential of $AgBiS_2$ nanocrystals, which exhibited broad absorption. Hence, more research attention should be devoted to developing favorable organic HTL materials and strategies for promising solar cells, e.g., polymer blending HTLs.

*Elevating device stability.* Stability is one of the critical factors for the commercial application of photovoltaic devices. PbS nanocrystal solar cells can retain over 90% of their initial performance after one year of ambient storage and ~80% of their initial efficiency after 1000 h of continuous illumination [19]. Nevertheless, $AgBiS_2$ nanocrystal solar cells suffer from rapid degradation due to inferior nanocrystal passivation and their unfavorable device structure. Wang et al. [6] recently demonstrated that $AgBiS_2$ nanocrystal solar cells with PTAA HTLs can retain ~80% of their initial performance after 40 h operation in ambient conditions, which mainly stemmed from the improved lattice ordering via cation disorder engineering. In addition, Oh et al. [12] revealed that the p–i–n structure can significantly enhance the ambient heating and water stability of $AgBiS_2$ nanocrystal solar cells over that with an n–i–p structure (Fig. 1e). Moreover, a bulk heterojunction can present superior stability over a conventional device structure with 90% retention of the initial performance after six months of ambient storage [18]. Despite this advancement, $AgBiS_2$ nanocrystal solar cells still present inferior stability compared to their PbS nanocrystal counterparts [6]. For instance, Sargent's group [20] demonstrated that PbS nanocrystal solar cells can retain >80% of their initial performance after 300 h of continuous operation in air. In this regard, more attention should be paid to developing better passivated $AgBiS_2$ nanocrystals and stable nanocrystal inks. One can also employ hydro/oxo-phobic organic HTLs for the ambient storage and stable operation of $AgBiS_2$ nanocrystal solar cells [19].

With these research efforts, $AgBiS_2$ nanocrystals are expected to experience a further rise in terms of photovoltaic performance and stability in the near future (Fig. 1f).

## Conflict of interest

The authors declare that they have no conflict of interest.

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## Appendix A. Supplementary materials

Supplementary materials to this perspective can be found online at https://doi.org/10.1016/j.scib.2023.01.031.

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Junwei Liu is currently a joint Ph.D. student in the groups of Profs. Zhihua Zhou and Long Ye at Tianjin University. He received his Bachelor's and Master's degrees from School of Environmental Science and Engineering, Tianjin University in 2016 and 2019, respectively. His research is focused on radiative cooling and low cost organic/hybrid solar cells.

Zhihua Zhou is a professor at Tianjin University. She received her Ph.D. degree from School of Environmental Science and Engineering, Tianjin University. Her current interest includes radiative sky cooling, renewable energy, and energy saving in buildings.

Long Ye has been a professor at School of Materials Science and Engineering, Tianjin University since 2019. He received his Ph.D. degree from Institute of Chemistry, Chinese Academy of Sciences in 2015. From 2015 to 2019, he was a postdoctoral researcher and later promoted to research assistant professor at the Department of Physics, North Carolina State University. His current interest includes organic/hybrid solar cells and energy conversion related applications.