Accepted Manuscript

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PII: S2095-9273(17)30125-1
DOI: http://dx.doi.org/10.1016/j.scib.2017.03.002
Reference: SCIB 77

To appear in: *Science Bulletin*

Please cite this article as: M. Lyu, L. Wang, Ternary solvent boosts two-dimensional perovskites, *Science Bulletin* (2017), doi: http://dx.doi.org/10.1016/j.scib.2017.03.002

Research Highlight

Ternary solvent boosts two-dimensional perovskites

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In the past few years, organic-inorganic/inorganic lead halide perovskites, most notably $CH_3NH_3PbI_3$ and its mixed cation/anion compounds, have attracted tremendous research interests in a wide range of different disciplines, which is largely initialized by their unprecedented success in low-cost and highly efficient solar cells. With certified efficiencies of over 22% in the lab-scale devices, lead halide perovskite solar cells have been considered as a serious rival of crystalline Si solar cells in the future photovoltaic market (http://www.nrel.gov/ncpv/images/efficiency_chart.jpg). The rapid progress in the lead halide perovskite solar cells has been relying on the confluence factors of their extraordinary intrinsic properties, including high light-absorption, low exciton binding energy, long charge carrier diffusion lengths, dominant shallow point defects, benign grain boundaries and ease of film crystallization via various low-temperature solution methods.[1-2] These excellent optoelectronic properties together with their prominent advantage of ease of fabrication have also endowed lead halide perovskites in a number of applications beyond photovoltaics, such as field-effect transistors, light-emitting diodes, photodetectors, lasers, X-ray detectors and memory devices, to name but a few.[3]

While the typical lead halide perovskites under the spotlight of research frontier adopt a three-dimensional (3D) structure, there is another class of two-dimensional (2D) counterparts that have recently attracted increasing research attention owing to their intriguing optoelectronic properties as well as superior ambient stability.[4] These layered perovskites share a general formula of $(R\text{-}NH_3)_2MX_4$, where R represents an organic functional group (e.g., alkyl or aromatic moiety), M is a divalent metal cation that is occupied with Pb in the lead halide perovskites, and X is a halide (e.g., Cl, Br or I). Layered structures of perovskites can be achieved by slicing their 3D compounds along certain crystallographic planes with tunable thickness of the inorganic layers. As the stability issue is one of the key challenges in the perovskite photovoltaic research that is currently limiting large-scale deployment and commercialization, the layered perovskites are emerging as a promising candidate in addressing this well-known stability issue.[4-5] Apart from their better stability, the layered perovskites are of great interest as an ideal paradigm for research of quantum

well due to their inherent semiconductor-insulator confined structures, in which only one/ few atomic layers of MX_4^{2-} framework are isolated by alkyl chains.[6] In addition, these 2D layered materials show anisotropic transport of charge carriers and strong excitons with large binding energies, which holds promise for a wide range of 2D material based applications and exciton related studies, respectively.[6] Motivated by their potential in both fundamental studies and practical applications, researchers have endeavored to develop and apply the layered halide perovskites with significant progress being achieved in the past few years.

In 2015, Yang and co-workers[7] reported a simple solution-phase growth of 2D single-crystalline perovskite ($(C_4H_9NH_3)_2PbBr_4$). This facile solution method leads to well-defined perovskites with only single/few unit-cell-thick 2D structures with interesting physical and optoelectronic properties.[7] Later on, Zeng's group reported the fabrications of atomically thin all-inorganic perovskites ($CsPbBr_3$) with a regular 2D nanosheet structure.[8] Excitingly, Mohite's group[9] subsequently demonstrated that perovskites with a 2D structure could possess both extraordinary optoelectronic performance and remarkably improved stability. Although 2D perovskites have since attracted enormous attention and witnessed rapid progress on their synthesis, and applications in solar cells, light-emitting diodes and a wide range of other applications over the past two years, the low-cost and facile fabrication of 2D perovskites with high quality still remains a big challenge due to the complexity in the wet-chemical processes.

In a latest work published on *Angewandte Chemie International Edition*, a systematic study on the ternary solvent assisted method has been reported for the controlled synthesis of 2D perovskites, which is a collaboration work between Zhai's group from Huazhong University of Science and Technology and Zeng's group from Nanjing University of Science and Technology.[11]

By employing a multi-step solution method with ternary solvent (Fig. 1a), they succeeded in developing ultrathin and large-sized 2D $(C_4H_9NH_3)_2PbBr_4$ cross stars by restraining the crystallization process of perovskites. They compared the crystallization morphologies of perovskites under various recipes of ternary solvent (dimethylformide, acetonitrile and chlorobenzene), and finally determined that acetonitrile played a crucial role in the formation of ultrathin 2D perovskites. It is found that the existence of acetonitrile can effectively suppress the growth of perovskites along the *c*-axis direction, which is resulted from the preferable absorption of –CN group on the crystal planes along the *c*-axis and thus leads to the ultrathin thickness of perovskites. In addition to acetonitrile, other polar solvents (e.g., alcohols) have a similar suppression effect on the crystallization process. On the other hand, the morphologies of perovskites are found to be strongly correlated with the supersaturation of precursor solutions (Fig. 1b). For example, perovskite precursors with low supersaturation generally induced shrinking thickness for resultant nanostructures. The special cross star shape is also a typical morphology for the

growth of perovskites dominated by diffusion effect. Careful control of the crystallization processes, they finally achieved 2D cross-star shaped $(C_4H_9NH_3)_2PbBr_4$ perovskites with lateral dimension up to 40 μm and only a few nanometers in thickness. More importantly, they also demonstrated that tunable optical properties of 2D $(C_4H_9NH_3)_2PbBr_xI_{4-x}$ perovskites can be achievable by rational iodide doping (Fig. 1c), which is of importance in applications of various optoelectronic devices.

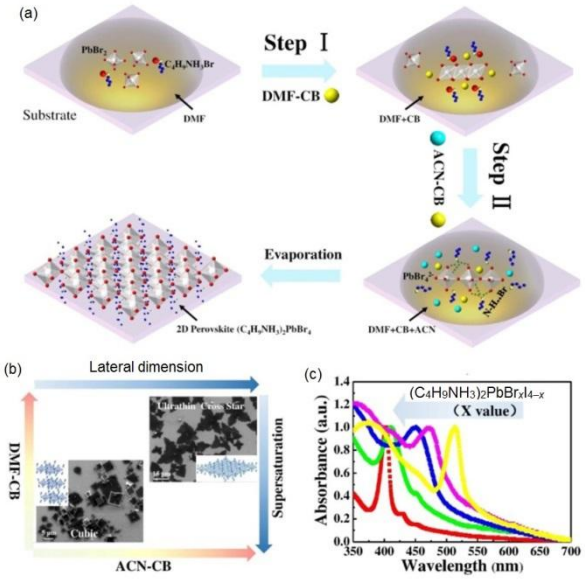

Fig. 1 (Color online) a) Multi-step solution processed method with ternary solvent for the fabrication of 2D $(C_4H_9NH_3)_2PbBr_4$ perovskite. b) Solvent volume ratio dependent morphology evolution of 2D $(C_4H_9NH_3)_2PbBr_4$ perovskite. c) Normalized absorption spectra of $(C_4H_9NH_3)_2PbBr_xI_{4-x}$ cross stars. Reprinted with permission from Ref. [11]. Copyright © 2017 John Wiley & Sons, Inc.

Wet-chemical synthesis of 2D perovskites is a very attractive strategy, which provides great potential for large scale fabrication of stable optoelectronic devices in the future. The work from Zhai and Zeng groups represents an important step forward on understanding and development of low-cost and stable 2D perovskites. However, it is of great interest to have more insight understanding on the roles of each solvent in the perovskite crystallization processes, to which end, the simulation method on a molecular level may be beneficial for supplementing the experimental techniques. We do expect to see more exciting fundamental progress as well as practical applications in the 2D perovskite based systems in the near future.

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