Lateral Epitaxial Heterostructures of Halide Perovskites for Diode Application

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Solution-processed lateral epitaxial growth of two-dimensional (2D) halide perovskite heterostructures, multiheterostructures, and superlattices is a daunting task because of their soft fragile ionic bonding and high intrinsic ion mobility of halide ions. Recently, these structures have been successfully developed for Pb²⁺- and Sn²⁺-based 2D halide perovskites using various large organic molecules, and its potential energy application has been shown in thin-film electrical diodes.

Different dimensional halide perovskites have shown their potential energy applications in various optoelectronic devices such as solar cells and light-emitting diodes (LEDs). Particularly, two-dimensional (2D) lead halide perovskites, first reported by Maruyama et al.,³ show intriguing properties such as excellent stability, multiple quantum well, and high power conversion efficiency.⁴,⁵ Integration of 2D perovskites with other materials such as graphene⁶ and transition metal halides⁷ opens up the new opportunity for building a wide variety of heterostructures for various energy applications. In 2000, Z. Alferov and H. Kroemer got the Noble Prize because of their notable contribution for the development of semiconductor-based heterostructures. These heterostructures show quantum wells, which lead the foundation of many modern electronic devices. However, there remains a big scientific knowledge gap about the layered halide perovskite (LHP) heterostructures, which could be the next big things in the energy field. A thin layer of organic molecules in LHPs gives better hydrophobicity, stability, and dense structures exhibiting quantum well properties. Thus, there is an urgent need for these kinds of heterostructures for commercialization of halide perovskite-based energy devices.

In the April 30, 2020 issue of Nature, Dou et al.⁸ reported the epitaxial growth of atomically sharp 2D perovskite heterostructure thin films via a solution phase sequential crystal growth approach (Figure 1A). The as fabricated heterostructures are tunable and thermally stable and show considerably suppressed amount of halide ion migration across the heterojunction. They used Pb²⁺/Sn²⁺ bromide and various ammonium salts such as bithiophenylethylammonium (2T⁺), butylammonium (BA⁺), phenylethylammonium (PEA⁺), quaterthiophenylethylammonium (4Tm⁺), 7-(thiophen-2-yl) benzothiadiazol-4-yl-[2,2’-bithiophen]-5-yl)ethylammonium (BTm⁺). All the prepared thin films were thoroughly characterized through photoluminescence (PL), X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM).

The authors showed that incorporation of rigid π-conjugated organic ligand in 2D perovskite heterostructure suppressed in-plane halide migration. They prepared two types of heterostructures with two different organic spacer ligands: a π-conjugated 2T⁺-based organic ligand and a non-conjugated linear BA⁺ ligand. Initially, very dilute precursor solution of bromide-based 2D perovskites was added on SiO₂/Si substrate to grow 2D sheets of perovskites given that it has a lower solubility in the quaternary solvent than the iodide-based 2D perovskites. Next, iodide solution of corresponding ligand and metal was added for lateral epitaxial growth of 2D sheets to form the 2D bromide perovskite (central layer)-2D iodide perovskite (peripheral layer) heterostructures. Thin films of these heterostructures exhibited distinct optical and PL images. The central bromide region of (2T)₂PbI₄-(2T)₂PbBr₄ showed no PL because of type-II band alignment between inorganic part and organic ligand,⁸ whereas the peripheral iodide region showed green PL at 515 nm because of type-I band alignment. In (BA)₂PbI₄-(BA)₂PbBr₄, the central bromide region showed blue emission at 411 nm and green emission at 515 nm in the peripheral iodide region. 2T⁺-based thin film exhibited almost similar PL spectra and image after 1 h heating at 100°C, whereas BA⁺-based thin film showed drastic change in emission spectra, and the PL image of the both green and blue region become quite faded. This phenomenon confirms the more significantly suppressed inter-diffusion of halide ions across the heterojunction of 2T⁺-based heterostructure than the BA⁺-based one due to presence of large conjugated ligands that inhibited the ion migration. Dou et al.⁸ used molecular dynamics simulation to examine the stabilization mechanism of halide migration across the heterojunction of both conjugated and non-conjugated ligand-containing 2D perovskites. It was shown that the amount of disorder at the interface is greatly affected by the nature of organic ligands present in the framework. The interface with the smaller non-conjugated ligand showed smaller degrees of disorder, thereby inhibiting halide migration. This work paves the way for the development of highly functionalized 2D heterostructures for various energy applications.
ligand showed increased disorder due to strain induced by lattice mismatch leading to halide anion inter-diffusion.

The characterizations of these heterostructures by TEM analysis were also a tedious task because these structures were grown directly on SiO2/Si substrates. To address this challenging issue, Dou et al.8 used a polymethyl methacrylate (PMMA) layer on top of growth substrate and then grew the heterostructures. Next, the PMMA layer was dissolved in chlorobenzene to obtain only the 2D heterostructures, which was easily transferred to the TEM grid. The authors also encountered structural damages, a common problem in all halide perovskites,9 of these films under the electron beam. They applied a minimum dose system to achieve crystal structure information, where focusing was done on an adjacent region of interest (ROI), so that the ROI would be less exposed directly to the electron beam. This technique will inspire others to obtain high-quality HRTEM images of hybrid perovskites.

In situ growth of 2D lateral heterostructures is always a challenging issue.10,11 Interestingly, using one-pot synthetic method, Dou et al.8 are also able to synthesize (2T)2PbI4–(2T)2PbBr4 lateral heterostructures, and this is attributed to the large solubility difference of these two 2D perovskites. Another striking phenomenon explored by the authors is periodic ripples that generally exist in robust heterostructure like WS2-WSe2.6 Here, periodic ripples with 5%–6% lattice strain are observed in (2T)2PbI4 region, which supports the coherency at the heterointerface in spite of weak and soft ionic nature of perovskite crystal lattice. Following their solution-phase epitaxial fabrication strategy, they also synthesized a series of multicomplex heterostructures as well as superlattices through variation of different halides, metal ions, and organic ligands shown in Figures 1B–1J. These findings will pave the design and synthesis of better heterointerface for optoelectronic devices.

As a proof of concept, Dou et al.8 fabricated atomically thin electrical diode based on variation of metal ions in the heterostructure and showed stable electrical rectifying behavior with enhanced exciton lifetime at the interface. The electrical diode based on the (4Tm)2SnI4-(4Tm)2PbI4 heterostructure showed a rectification ratio of around 102 without any hysteresis. These results are quite promising for diode applications of these new materials.

Overall, the present study opens up new possibilities for creating a large variety of unique materials for optoelectronic applications.
devices. Of course, the reproducibility of various materials along with large-scale production of uniform heterostructures should be achieved by various groups for its practical applications.


