Composition Engineering in Two-Dimensional Pb–Sn-Alloyed Perovskites for Efficient and Stable Solar Cells

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ABSTRACT: Environmentally friendly tin (Sn)-based metallic halide perovskites suffer from oxidation and morphological issues. Here, we demonstrate the composition engineering of Pb–Sn alloyed two-dimensional (2D) Ruddlesden–Popper perovskites, (BA)$_2$(MA)$_3$Pb$_{3–x}$Sn$_x$I$_{13}$ for efficient and stable solar cell applications. Smooth thin films with high surface coverage are readily formed without using any additive owing to the self-assembly characteristic of 2D perovskites. It is found that Sn plays a significant role in improving the crystallization and crystal orientation while narrowing the bandgap of Pb–Sn 2D perovskites. Photophysical studies further reveal that the optimal Sn ratio (25 mol %) based sample exhibits both minimized trap density and weakened quantum confinement for efficient charge separation. Consequently, the optimized (BA)$_2$(MA)$_3$Pb$_{1–x}$Sn$_x$I$_{13}$-based solar cells yield the best power conversion efficiency close to 6% with suppressed hysteresis.

KEYWORDS: organic–inorganic hybrid perovskites, two-dimensional, tin-based perovskites, composition engineering, planar solar cells

Organic–inorganic lead halide perovskite solar cells are excellent candidates for solution-processable thin-film solar energy conversion owing to the impressively boosted power conversion efficiencies (PCEs) from 3.8 to 22.1% in the past several years. However, the environmental toxicity of lead severely limits the further commercialization. Thus, the development of eco-friendly lead-free or -less alternatives is highly imperative. For instance, germanium(II) (Ge$^{2+}$), tin(II) (Sn$^{2+}$), antimony(III) (Sb$^{3+}$), and bismuth(III) (Bi$^{3+}$) have been employed to replace Pb$^{2+}$ completely or partially. Among them, Sn-based perovskites gave rise to narrower optical bandgaps ($E_g$), which have thus far achieved reasonably the best device performance. Noticeably, in 2014, CH$_3$NH$_3$SnI$_3$ perovskite solar cells demonstrated the PCEs of 5–6%. Following those work, a variety of strategies, such as the addition of SnF$_2$ and pyridine, have been attempted to further improve the cell performance, which was however not successful. The critical challenge of retarding the device improvement lies mainly in the facile oxidation of Sn$^{2+}$ to Sn$^{4+}$, which causes detrimental p-type self-doping and decreases the diffusion lengths of photoexcited carriers. Another limiting factor is the uncontrollable film morphology of Sn-based perovskites owing to the fast crystallization between SnI$_2$ and methylammonium iodide.

The emerging two-dimensional (2D) Ruddlesden–Popper perovskites have been demonstrated to exhibit appealing environmental stability owing to the hydrophobic nature of their insulating organic spacers, which prevents the penetration of water and oxygen molecules and might help to resolve the oxidation issue of Sn-perovskites. Moreover, they possess good capability of self-assembly, which ensures the formation of high-quality film without the need of any additive. However, the insulating organic spacers also lead to the unfavorable large $E_g$ for Pb-based 2D perovskites. The inclusion of Sn can resolve this issue, as demonstrated in the case of three-dimensional (3D) perovskites. Yet, to the best of our knowledge, there only exists a few reports on Sn-based 2D perovskites. For example, Adachi et al. successfully applied (C$_6$H$_5$)$_2$NH$_2$SnI$_4$ to field-effect transistors, which exhibited a record hole mobility of 15 cm$^2$/V s at room temperature. Very recently, Kanatzidis et al. reported two series of new Sn-based 2D perovskites, (HA)Pb$_{1–x}$Sn$_x$I$_4$ and (BZA)$_2$Pb$_{1–x}$Sn$_x$I$_4$, where HA and BZA stand for histammonium and benzylammonium cations, respectively. These two systems displayed a varying trend of $E_g$ with an increasing Sn fraction. Later, the same group for the first time employed (BA)$_2$(MA)$_{n–1}$SnI$_{3n+1}$ as the photoactive layer in solar cells. By using triethylphosphine additive, the oxidation of Sn$^{2+}$ was
suppressed and a PCE of 2.5% was obtained for those of \( n = 4 \).\(^{23}\) However, this performance is still poor as compared to Pb-based counterparts.

In this work, we develop Pb- and Sn-alloyed 2D perovskites, \((BA)_{2}(MA)_{3}Pb_{4−x}Sn_{x}I_{13}\) for planar solar cell applications. On the one hand, the self-assembly characteristic of 2D perovskites gives rise to the formation of high-quality \((BA)_{2}(MA)_{3}Pb_{4−x}Sn_{x}I_{13}\) films without the aid of any additive. On the other hand, the addition of Sn diminishes the use of Pb to some extent, which is more environment friendly. Furthermore, it greatly reduces \( E_{g} \) enhances light absorption, and improves charge transport when comparing to analogous Pb-based 2D perovskites. Therefore, such alloyed Pb–Sn devices afford the best PCE of 5.96% when the molar ratio of Pb/Sn = 3:1.

Five sets of \((BA)_{2}(MA)_{3}Pb_{4−x}Sn_{x}I_{13}\) 2D perovskites were obtained by the one-step spin-coating method. The precursor solutions were prepared by mixing PbI\(_{2}\), SnI\(_{2}\), C\(_{4}\)H\(_{9}\)NH\(_{2}\), HI, and CH\(_{3}\)NH\(_{3}\)I at a stoichiometric ratio of \( 4 = x:2:2:3 \) \((x = 0, 1, 2, 3, 4) \) in dimethyl formamide, which corresponds to Pb/Sn = 4:0, 3:1, 2:2, 1:3, 0:4. We first conducted the X-ray diffraction (XRD) measurement to study the effect of Sn substitution on crystal phases of these 2D perovskites. The initial \((BA)_{2}(MA)_{3}Pb_{4}I_{13}\) perovskite displays exclusively two weak diffraction peaks at 14.35 and 28.51°, which are assigned to characteristic (111) and (202) lattice planes of 2D perovskites, respectively (see Figure S1 in Supporting Information).\(^{18}\) As shown in Figure 1a, when Pb is partially replaced by Sn, the peak intensity is remarkably increased, implying that the insertion of Sn can significantly enhance the crystallization of 2D perovskites. The corresponding spectral expansions in the diffraction regions of 14.5–15.0 and 27.2–29.2° are shown in Figure 1b. As the Sn ratio increases, both (111) and (202) planes are gradually up-shifted toward high angles. This indicates the conversion of Pb-based perovskites to Sn-containing counterparts where the parameters of unit cells become smaller, which is in good accordance with previous report.\(^{22}\) In particular, two additional peaks around 13.8 and 27.7° appear when the Sn fraction is increased up to 75 and 100%, suggesting the formation of second phases, which may be ascribed to the oxidation of Sn\(^{2+}\) to Sn\(^{4+}\).

Figure 2 compares the optical absorption spectra of these alloyed Sn–Pb 2D perovskites \((BA)_{2}(MA)_{3}Pb_{4−x}Sn_{x}I_{13}\) and their corresponding \( E_{g} \)s are displayed in Figure S2. With increasing Sn proportions, the absorption spectra continuously red shift. As a result, the decreasing \( E_{g} \) values are estimated for \((BA)_{2}(MA)_{3}Pb_{4}I_{13}, (BA)_{2}(MA)_{3}Pb_{3}SnI_{13}, (BA)_{2}(MA)_{3}Pb_{2}Sn_{2}I_{13}, (BA)_{2}(MA)_{3}PbSn_{3}I_{13}, \) and \((BA)_{2}(MA)_{3}Sn_{4}I_{13}\) to be 2.09, 2.01, 1.79, 1.77, and 1.67 eV, respectively.

We then examined the film morphology by using field-emission scanning electron microscopy (FE-SEM). It can be seen that the \((BA)_{2}(MA)_{3}Pb_{4}I_{13}\) film is very smooth (Figure 3a), whereas an incorporation of Sn makes the film become textured due to the increasing crystallization. At the Sn fraction of 25 mol %, the film consists of crystal grains with an average size of 150 nm (Figure 3b). When the Pb/Sn = 2:2 mol %, the film gets coarse and rectangular grains show up (Figure 3c). As the Sn content continues to increase, the crystals seem to merge with each other, accompanied by pinholes, which are detrimental to device performance (Figure 3d,e). Subsequently, we performed grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement. As shown in Figure 2f, the neat Pb-based perovskites display continuous rings, whereas the Sn–Pb analogs exhibit discrete spots (Figure 2g–j). This indicates a significant improvement of both crystallization and crystal orientation upon the inclusion of Sn, which is consistent with XRD results.

Given these favorable optical and crystalline characteristics, we fabricated planar solar cells with a normal device structure of ITO/PEDOT:PSS/(BA)\(_{2}(MA)_{3}Pb_{4−x}Sn_{x}I_{13}/PCBM/Bphen/Al, as schematically shown in Figure 4a. Figure 4b presents the current density versus voltage \((J−V)\) curves of \((BA)_{2}(MA)_{3}Pb_{4−x}Sn_{x}I_{13}\)-based planar photovoltaic cells measured under illumination by a calibrated AM 1.5G solar simulator at reverse scan. The detailed photovoltaic parameters of these four group devices are summarized in Table 1. The device based on neat Pb-based 2D perovskite counterparts exhibits a PCE of 3.61%. As the Sn content is increased, the open-circuit voltage
The Voc of the cells is gradually decreased, which can be attributed to the reduced Eg of Sn-based 2D perovskites, as indicated from their absorption spectra. Meanwhile, the short-circuit current (Jsc) first increases when Pb/Sn = 3:1 and then decreases when the Sn content is larger than 25%. The increased Jsc in (BA)2(MA)3Pb4−xSnxI13-based devices is attributable to the enhanced light absorption, whereas the decreased Jsc for other Sn-based samples originates presumably from those traps generated by second phases, as shown in XRD patterns. As a result, the optimal (BA)2(MA)3Pb4−xSnxI13-based device yields the best PCE of 5.96% with large Voc = 0.80 V, Jsc = 12.05 mA/cm², and FF = 61.81%. The increased Jsc in (BA)2(MA)3Pb4−xSnxI13-based devices is attributable to the enhanced light absorption, whereas the decreased Jsc for other Sn-based samples originates presumably from those traps generated by second phases, as shown in XRD patterns. As a result, the optimal (BA)2(MA)3Pb4−xSnxI13-based device yields the best PCE of 5.96% with large Voc = 0.80 V, Jsc = 12.05 mA/cm², and FF = 61.81%. Figure 4c displays the external quantum efficiency (EQE) profiles of (BA)2(MA)3Pb4−xSnxI13-based devices. Their integrated current densities are 4.50, 8.13, 4.68, and 1.81 mA/cm² for x = 0, 1, 2, and 3, respectively, which are in accordance with the Jsc varying trend despite that the values are comparatively lower.
out that the (BA)₂(MA)₃Pb₃SnI₁₃-based device displays the
that in 3D perovskites devices, implying that the oxidized
varied Sn ratios. The mobility value is also on the same order as
conclude that such interaction in this work is insensitive to the
Sn⁴⁺ species and insulating organic spacers of 2D Pb
introduction of Sn can slightly suppress bimolecular recombi-
Figure 5. (a–e) TA spectra at selected delay time after light excitation for (BA)₂(MA)₃Pb₄⁻Sn⁻SnI₁₃ perovskites with (f–j) corresponding SVD global
photoluminescence (TRPL) measurements on neat films were
for 2D perovskites with various Pb/Sn ratios. They are
constituted of multibleach bands, which correspond to the
state filling of 2D quantum wells with different thicknesses of
inorganic layer. When the Sn faction is more than 50%, the
majority of charge carriers tend to reside at the thinner
quantum well phase (smaller n), as indicated by the negative
bleach bands in Figure 5c–e. Consequently, the larger exciton
binding energy in thin quantum wells would hinder charge
dissociation. This could be one of the origins for the low
photocurrent in the devices with larger Sn content. We then
performed the singular value decomposition (SVD) fitting of
the TA spectra to obtain the excited state lifetime, as
summarized in Figure 5f. In general, the TA spectra can all
be fitted by one fast (3−31 ps) component and the other slow
(0.1−12 ns). The fast component can be attributed to the
biexciton recombination (i.e., bimolecular recombination, see
Figure S6 for details). The relative amplitude of the fast
component over the slow one first decreases and then increases
with increasing Sn ratio, where the lowest value occurs at the
Pb/Sn ratio of 3:1. This confirms the above argumentation
from Figure 4d that the bimolecular recombination can be
surpassed by the 25% Sn addition.
To assign the slow component in TA dynamics, we also
performed the TRPL measurement of identical samples, and
the results are shown in Figure 6. The PL decays can be well
fitted by biexponential functions, as summarized in Table S2.
We found that the lifetimes of dominate slow component in
TRPL is consistent with the slow components extracted from
TA in Figure 5f−j. This indicates that the slow component in
TA can be assigned as first-order recombination of singlet
excitons. Such single excitation state lifetimes exhibit the
consistent dependence on Sn ratio with that of device
performance, as shown in Figure 5f−j, where the sample with
Pb/Sn = 3:1 shows the longest lifetime of 12 ns. This indicates
that the trap densities within the lattice are minimized.
In Pb–Sn mixed 3D perovskite-based solar cells, the device performance is concurrently affected by the Sn addition through three ways: (1) the lattice distortion that induces trap states, (2) $E_g$ that is tunable by competition of spin-orbit coupling between Pb$^{2+}$ and Sn$^{2+}$ ions, and (3) charge carrier mobilities that are modulated by carrier–lattice interaction. In 2D perovskites, as the quantum confinement of 2D perovskites restrict the uplimit of carrier mobilities in the range of 1–2 cm$^2$/(V s)$^{-1}$, there is little room for the Sn substitution to tune the intrinsic carrier transport capability by changing the carrier–lattice interaction. On the other hand, the Sn addition greatly dominates the assembly of 2D quantum wells and affects the $n$ value. Although the underlying synthetic mechanism remains to be discovered, the Sn addition below 50 mol % would formulate the majority 2D phases with the maximum quantum well thickness ($n = 3$ or 4), which facilitates exciton dissociation as well as charge transport. Moreover, the trap densities within 2D perovskites are dominated by the Sn addition. As the structural distortion in Sn-based perovskites is generally less than that in Pb-based analogs, the initial Sn addition is expected to diminish the lattice deformation. However, the rearrangement of 2D quantum wells induced by further Sn addition would increase trap densities. As a result, the trap density of the optimal Sn ratio (25 mol %) based sample with the best solar cell performance is much less than that in 3D perovskites counterparts (60–80 mol %). This can also account for the improved stability for the (BA)$_2$(MA)$_3$Pb$_2$Sn$_{1-x}$I$_{3}$-based device.

To conclude, we have demonstrated the solar cell applications of Pb–Sn-allayed 2D perovskites. As compared to neat Pb counterpart, (BA)$_2$(MA)$_3$Pb$_{2-x}$Sn$_x$I$_3$ 2D perovskites exhibit significantly enhanced optical absorption, crystallization, and crystal orientation. Moreover, the film morphology is notably improved in comparison to traditional Sn-based 3D perovskites, which can be ascribed to the self-assembly characteristic of 2D perovskites. The composition-optimal (BA)$_2$(MA)$_3$Pb$_2$Sn$_{1-x}$I$_3$-based regular planar solar cell yields the best PCE up to ~6%. Importantly, time-resolved spectroscopical studies reveal that the lattice mismatch in optimized devices has been minimized with less trap centers and longer charge carrier lifetime, whereas the thickness of the quantum wells is maximized with more efficient charge separation and transportation. This work exemplifies an effective avenue toward efficient, stable, and eco-friendly 2D Pb-less perovskite solar cells.

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