2D homologous organic-inorganic hybrids as light-absorbers for planer and nanorod-based perovskite solar cells

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ABSTRACT

We present the fabrication and characterization of two dimensional (2D) perovskites $(PEA)_2(MA)_{m-1}Pb_mI_{3\ m+1}$ (PEA=phenylethylammonium, MA=methylammonium, m=1,2,3) for application as light absorbers in solar cells. Films of 2D perovskite series show high stability under humid air, with band gaps decreasing with increasing m values, from 2.36 eV for $(PEA)_2PbI_4$ (m=1) to 1.94 eV for $(PEA)_2(MA)_2Pb_3I_{10}$ (m=3). Owning to the smaller bandgap, favorable vertical growth characteristics, and appropriate energy band structure of $(PEA)_2(MA)_2Pb_3I_{10}$, planer perovskite solar cells based on $(PEA)_2(MA)_2Pb_3I_{10}$ exhibit best cell performance. Incorporation of TiO_2 nanorod arrays into $(PEA)_2(MA)_2Pb_3I_7$ based perovskite solar cells are further found to be useful in improving the cell performance, ascribing to the improved quality and coverage of the perovskite films, as well as the enhanced electronic contact between the perovskites and the electron transporting layer. By optimizing the TiO_2 NR lengths, an efficiency of 3.72% is obtained for $(PEA)_2(MA)_2Pb_3I_{10}$ perovskite cells with 600 nm-long TiO_2NRs as scaffolds, which is more than a time higher than that of the planer analogue device. Our study to design 2D perovskite solar cells demonstrates the importance of material structure and device configuration for efficient solar cells, highlighting the validity of TiO_2 nanorods in functionalizing 2D perovskites for photovoltaic applications.

1. Introduction

Three-dimensional (3D) lead halide based perovskites are emerging as one of the most promising light absorbers in recent years [1–7]. Rapid material and device optimization has led to their power conversion efficiency (PCEs) exceeding 20% in just a few years [8–10]. Among the perovskite choices, methyl ammonium lead iodide ($MAPbI_3$) has become the archetypal light absorber due to its solution process-able, high extinction coefficient [11], medium band gap [12], small exciton binding energy [13], and long exciton and charge diffusion lengths [14,15]. Although considerable progress has been made in improving the PCEs in perovskite solar cells, these cells still suffer from the moisture instability issue, which is mainly associated with phase transitions and ambient hydrolysis of $MAPbI_3$ [16]. Great efforts, such as improving the crystallinity and quality of perovskite films [17], partial or fully replacing MA^+ with formamidinium (FA^+) [6,9,18], substitution I^- with Br^- [19],Cl^- [20], or pseudo-halide SCN^- [21–24], regulating the morphology and crystallinity of the contacting electron transport layers (ETLs) [25,26], or adding a buffer layer [16,27] or an encapsulation layer atop [28] are devoted to enhance the

stability as well as the efficiencies of the perovskite solar cells. Nevertheless, the moisture sensitivity of 3D $MAPbI_3$-based compounds has not been substantially addressed yet.

It is therefore of great importance to study and develop alternative classes of moisture resistant perovskite compounds for photovoltaic applications. Recently, attempts to utilize two-dimensional (2D) layered hybrid compounds in perovskite solar cells have been made with pioneering progress [29–36]. For example, Smith I.C. et al. reported the solar cell application of a layered $(PEA)_2(CH_3NH_3)_2Pb_3I_{10}$ (where PEA=phenylethylammonium) perovskite light absorber, demonstrates an open-circuit voltage of 1.18 V and a power conversion efficiency of 4.73% [29]. More importantly, it is relatively stable in air containing 52% relative humidity for up to 46 days. Cao et al. reported that 2D perovskites existing in the system of $(n-C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$(n=1–4) are suitable as moisture resistant absorbers for solar cells [30], exhibiting an initial power conversion efficiency of 4.02% from the n=3 compound. Moreover, lead-free layered perovskite derivative $Cs_3Sb_2I_9$ [31] and $(CH_3NH_3)_2CuCl_xBr_{4-x}$ [32] are synthesized with the aim of investigating the film formation for technological applications and studying the optoelectronic properties to explore their potential as light

harvesters in solar cells. Very recently, Mitzi D.B. explored the photovoltaic-relevant properties of 2D $MA_2Pb(SCN)_2I_2$ perovskite, predicting its use as an absorber for the top cell of a tandem solar cell [33]. Although no superior device performance has been obtained yet, such 2D layered hybrids would lead to versatile approaches for the applications of novel perovskite films with adjustable optoelectronic properties and enhanced air stability [29,30,34].

As we know, 2D layered perovskites, which can be structurally derived by cutting the 3D analogue along specific orientations and piling up alternating organic and inorganic slabs, affords greater tunability, moisture resistance, and processing property on thin film deposition [11,37]. To move from the 3D to the 2D perovskites, the small MA^+ cation is replaced by a much bulkier organic primary ammonium cation, thus confining the perovskite in two dimensions because of steric effects. The spatial quantum confinement of the 2D sheets leads to strongly bound excitons because of large differences in the band gaps of inorganic and insulating organic layers as well as their large dielectric mismatch ($\varepsilon_{org} < _{inorg}$) [38]. Such tightly bound excitons are difficult to dissociate into free charge carriers at room temperature, and hence free charge carriers are not likely to reach the electron/hole selective contacts [29]. Therefore, before the year of 2014, 2D perovskites are normally considered to be of little use for light harvesting, and are mainly employed in field-effect transistor and light-emitting diode devices. However, a recent study by Ahmad S. et al. reveals that excitons in 2D perovskites strongly contribute to the photocurrents despite possessing binding energies over 10 times larger than the thermal energies [39]. The extracted photocurrents can be further enhanced by 100-fold by incorporating electron- and hole-transport layers, demonstrating the far more efficient exciton dissociation and carrier transport in these 2D materials than was expected from previous considerations. Their results suggest that strong excitonic materials may be also useful as photovoltaic materials despite high exciton binding energies.

In previous reports about 2D perovskites related solar cells, two main device configurations have been explored: the mesoscopic nano-particulate structure and the planar heterojunction structure. The demonstration of other nanostructures such as vertical nanorods as scaffold for 2D perovskites solar cells has not been addressed till now. Metal oxide nanorods, which offer improved percolation paths, enhanced electron mobility and light trapping effect, are of great research interest as a scaffold in the community of nanostructured solar cells [40–42] and photocatalysts [43–47]. With the above considerations in mind, we turned our attention toward the potential of 2D homologous organic-inorganic multilayered perovskite hybrids as light-absorbing materials and the correlation of their photovoltaic properties with the scaffold layer morphology.

In this study, thin films of 2D lead iodide perovskite $(PEA)_2(MA)_{m-1}Pb_mI_{3m+1}$ (m=1,2,3, m stands for the number of Pb-I sheets in each inorganic slab) series and were readily formed by one-step spin coating from a DMF precursor combining (PEA)I, (MA)I, and PbI_2 in stoichiometric ratios under ambient conditions. Effects of the m value on the orientation, morphology, bandgaps and energy band structure of the hybrid films are investigated. Two types of architectures were designed for the $(PEA)_2(MA)_{m-1}Pb_mI_{3m+1}$ based solar cells: (i) planar devices employing a TiO_2 compact layer (CL, ~60 nm), (ii) devices employing TiO_2 nanorods (NRs) scaffold (~350–800 nm). For the m=3 multilayered $(PEA)_2(MA)_2Pb_3I_7$ hybrids that featuring a favorable vertical growth characteristic, the NRs device showed enhanced performance as compared to the planer device, which could be ascribed to better quality of the resulting hybrid films and the enhanced electronic contact and charge extraction from the inorganic sheets to the electron transporting layer. With process optimization, we have been able to obtain energy conversion efficiency of 3.72% for cells with 600 nm-long TiO_2 NRs. The insights gained from this work demonstrate a proof of concept that the homologous 2D halide perovskites are stable and promising light-absorbing

materials, highlighting the importance of material structure and device engineering for efficient solar cells.

2. Experimental section

2.1. Materials

Commercially available lead iodide (PbI_2, 99.99%, Sigma-Aldrich), β-phenylethylamine (PEA, 98%, Aladdin), methylamine (MA, 30 wt% in ethanol, Aladdin), hydriodic acid (HI, 57% in water, Sigma-Aldrich), 2,2,7,7′-Tetrakis(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene(spiroMeOTAD, 99.5%, Lumtec.) were used as received. Methylammonium iodide (MAI) or phenylethylammonium iodide ((PEA)I) was synthesized by dropwise adding a 57% w/w aqueous HI to equimolar amounts of 30% w/w MA or 98% PEA. After stirring at 0 °C for 2 h, the resulting solutions were evaporated at 50 °C for 1 h to precipitate MAI and (PEA)I, respectively. The precipitates were washed three times with diethyl ether and dried under vacuum and used without further purification.

2.2. Substrate preparation

FTO-coated glass (1.5 cm×1.5 cm, 15 Ω sq^{-1}) was patterned by etching away a 3 mm strip with zinc powder and 4 M HCl. Then, substrates were ultrasonically cleaned with detergent, acetone, and isopropanol. After cleaned by the UV-Ozone machine, a ~60 nm TiO_2 CL was deposited by sequentially spin-coating 0.15 M and 0.30 M n-butylalcohol solution of titanium diisopropoxide bis(acetylacetonate) at 3000 rpm for 30 s. The substrate were dried at 125 °C for 10 min after the first coating, and annealed at 500 °C for 30 min after the second coating. For planar structure devices, the substrates were then soaked in a 40 mM aqueous solution of $TiCl_4$ for 30 min at 70 °C, rinsed with deionized water, and annealed at 500 °C for 20 min. For NRs device, TiO_2 NRAs were hydrothermally grown on the TiO_2 CL following the reported procedure [40,41]. In brief, the substrates with TiO_2 compact layer were placed up-side down in a sealed Teflon reactor (100 mL), containing 30 mL of deionized water, 30 mL of hydrochloric acid (37 wt%), and 0.6 mL of tetrabutyl titanate. The reactor was placed inside an oven preheated to 150 °C. The reaction time was set to 4, 5, and 6 h to get the desired TiO_2 NR lengths. The reactor was cooled rapidly to room temperature under flowing water. The substrates were removed from the reactor, rinsed and dried.

2.3. 2D Perovskite films deposition and device fabrication

The $(PEA)_2(MA)_{m-1}Pb_mI_{3\ m+1}$ family of perovskite hybrid films were deposited on TiO_2 CL or NRAs by the spin-coating method. The corresponding precursor solutions (1.0 M Pb^{2+}) of $(PEA)_2(MA)_{m-1}Pb_mI_{3\ m+1}$ with different m value were prepared by stoichiometrically mixing the readily synthesized MAI, (PEA)I and PbI_2 in anhydrous N,N-dimethylformamide (DMF) and filtered through a 0.45 μm PVDF syringe filter. The solutions were deposited on the substrate (60 μL) and spun at 3000 rpm for 30 s. 2D perovskite films were formed immediately after spin-coating at room temperature.

To fabricate 2D perovskite solar cells, the spiroOMeTAD hole-transporting material (HTM) solution, which was prepared by dissolving 83.2 mg spiroOMeTAD, 15.62 μL of a stock solution of 500 mg mL^{-1} lithium bis(trifl uoromethylsulphonyl)imide in acetonitrile and 33.76 μL 4-tert-butylpyridine (Sigma-Aldrich) in chlorobenzene (1.0 mL), was deposited on the light-absorbing $(PEA)_2(MA)_{m-1}Pb_mI_{3m+1}$ perovskite layer by spin-coating at 4000 rpm for 30 s. Finally, a 60 nm-thick gold layer was deposited by thermal evaporation on the spiroOMeTAD layer as a back contact.