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Precursor effects on methylamine gas-induced $CH_3NH_3PbI_3$ films for stable carbon-based perovskite solar cells

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ABSTRACT

Carbon-based perovskite solar cells (PSCs) without hole transport material have attracted much attention due to their high stability. However, their power conversion efficiency (PCE) is still low because of the lack of suitable perovskite deposition methods. In this work, a facile solid-gas reaction method was explored to prepare high quality perovskite and the effects of precursor composition (PbI_2, PbI_2 + HI, $HPbI_3$ and PbI_2 + NH_4I) on the CH_3NH_2 (MA) gas-induced perovskite were systematically investigated. The lack of H^+/I^- and/or HI suppressed the conversion of PbI_2 precursor to $MAPbI_3$, while rapid and complete conversion was achieved for (PbI_2 + HI), $HPbI_3$ and (PbI_2 + NH_4I) precursors. Compared with $HPbI_3$ precursor, the presence of H_2O molecules in (PbI_2 + HI) precursor lowered the perovskite crystallinity, while the release of NH_3 from (PbI_2 + NH_4I) precursor slower the interaction of MA molecules with $MAPbI_3$ for achieving the highest quality $MAPbI_3$ layer. The application of an anti-solvent treatment during precursor deposition further improved the quality of $HPbI_3$ and (PbI_2 + NH_4I)-processed perovskite layers, which as a result, significantly promoted the photovoltaic performance of C-PSCs. Both devices exhibited considerably high stability, especially for the (PbI_2 + NH_4I)-processed C-PSCs, who did not show any PCE degradation after storage in air atmosphere at room temperature for 120 days.

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted much attention because the high power conversion efficiency (PCE) could be achieved by solution-based techniques (Kojima et al., 2009; Im et al., 2011a; Kim et al., 2012; Burschka et al., 2013; Zhou et al., 2014a; Yang et al., 2015; Bi et al., 2016; Yang et al., 2017; Abdijalebi et al., 2018; Zeng et al., 2017; Im et al., 2011b). However, the stability of the traditional PSCs is still too low for practical application, which is attributed not only to the inherent properties of organic-inorganic hybrid perovskite materials but also to the instable and air-sensitive hole transport materials (HTMs) (Niu et al., 2014; Wang et al., 2016). Fortunately, it was found that perovskite could serve as both light absorber and hole transporter (Kim et al., 2012; Stranks et al., 2013; Etgar et al., 2012), and HTM-free PSCs also worked efficiently (Stranks et al., 2013; Etgar et al., 2012; Aharon et al., 2014; Laban and Etgar, 2013; Xing et al., 2013). So far, several kinds of electrodes have been employed to directly extract holes from perovskite layers, including Au (Etgar et al., 2012; Laban and Etgar, 2013), Ni (Ku et al., 2015), and carbon (Ku et al., 2013; Wei et al., 2014; Chen et al., 2014; Chen and Yang, 2016). Among them, carbon seems to be the most promising one as it is cheap, stable, inert to ion migration and inherently water-resistant (Chan et al., 2016; Chen et al., 2014, 2015, 2016; Chu et al., 2018; Hashmi et al., 2017a, 2017b; Li et al., 2016; Liao et al., 2018; Liu et al., 2015; Tsai et al., 2017; Zheng et al., 2016; Zhou et al., 2014b), and carbon-based HTM-free PSCs (C-PSCs) have shown significantly high stability. However, the PCE of lead-based C-PSCs is still considerably lower than that of HTM-based PSCs.

As the light absorber and hole transporter in C-PSCs, the perovskite film greatly influences device performance. Since a relatively thick TiO_2 mesoporous scaffold (400–1000 nm) is necessary in C-PSCs for efficient charge separation, the deposition strategies of the perovskite layers are different from those used for HTM-PSCs (Qureshi et al., 2016). One-step deposition method that has been widely used in HTM-PSCs (Conings et al., 2014; Gaspera et al., 2015; Kim et al., 2013; Li et al., 2015; Liang et al., 2014; Wang et al., 2014; Zhao and Zhu, 2014) is usually faced with poor pore filling in the thick TiO_2 mesoporous scaffold. Two-step deposition method partially solves the problem mentioned above because the volume expansion at the second conversion step could improve the pore filling. Nevertheless, it is hard to completely convert a precursor to perovskite, while a longer immersion duration in reaction solution tends to induce the Ostwald ripening that would lower crystal

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quality. To avoid incomplete conversion and Ostwald ripening, new conversion processes should be developed. Gas phase-based conversion process is a good choice, but temperature over 150 °C was usually needed to evaporate MAI gas, which is detrimental to perovskite crystals (Dualeh et al., 2014; Yan et al., 2015). Recently, methylamine (MA) gas treatment that was conducted at low temperature has been explored as the second step to prepare perovskite layers for HTM-based PSCs (Hong et al., 2017; Raga et al., 2017; Zhang et al., 2016; Zhou et al., 2015). Pang et al. (2016a) have treated $HPbI_3$ crystals with MA gas to form $MAPbI_3{\cdot}xCH_3NH_2$ liquid intermediate. After being taken out from MA atmosphere, excess MA molecules were released from the intermediate to produce $MAPbI_3$. Similar phenomenon was also observed when NH_4PbI_3 was used as precursor by Zong et al. (2016). The liquid intermediate not only promoted full conversion and improved crystal quality in thick TiO_2 scaffold, but also significantly reduced the surface roughness of the perovskite layers. For the promising paintable C-PSCs (device structure: FTO/TiO_2 compact layer/TiO_2 mesoporous layer/perovskite/carbon), carbon electrode is commonly coated on a pre-deposited perovskite layer. The poor contact at the perovskite/carbon interface greatly suppresses photovoltaic performance. The smoother perovskite layer obtained by the MA gas treatment would lead to a better interface contact with carbon electrode and higher device performance. Therefore, MA gas treatment seems to be a promising process to deposit high-quality perovskite layers in the thick TiO_2 mesoporous scaffolds for the C-PSCs, especially for the paintable C-PSCs.

Herein, MA gas treatment process has been adopted as the second step to convert a precursor layer to perovskite layer for the printable C-PSCs. The effects of different precursors (PbI_2, PbI_2 + HI, $HPbI_3$ and $PbI_2 + NH_4I$) on the composition and morphology of MA-gas induced $MAPbI_3$ layers and the performance of the C-PSCs were systematically investigated. A large difference in composition, crystallinity and morphology was found for the perovskite layers obtained from different precursors, which was attributed to the diversity in reaction process and mechanism. The complete and rapid conversion was achieved for the (PbI_2 + HI), $HPbI_3$ and ($PbI_2 + NH_4I$) precursors, and the ($PbI_2 + NH_4I$)-processed perovskite layer exhibited the highest crystallinity and quality due to the absence of H_2O molecules and the slow interaction of MA molecules with $MAPbI_3$. By further applying an anti-solvent treatment during the spin-coating, the quality of the ($PbI_2 + NH_4I$)-processed perovskite layer was further improved. The C-PSCs based on the NH_4PbI_3-procssed perovskite layer achieved a highest PCE of 11.64%. Furthermore, after storage in air atmosphere for 120 days at room temperature (humidity ~ 10–20%), the ($PbI_2 + NH_4I$)-processed C-PSCs did not exhibit any PCE degradation.

2. Results and discussion

Four different precursor solutions were prepared by dissolving PbI_2, (PbI_2 + HI), $HPbI_3$ and ($PbI_2 + NH_4I$) in DMF (Fig. 1a_1–d_1), respectively. Pb-I precursor layers were deposited by spin-coating the different precursor solutions on TiO_2 mesoporous scaffold. The Pb-I precursor layers were then converted to $MAPbI_3$ perovskite layers in a MA atmosphere. As shown in Fig. 1a_2–d_2, PbI_2, (PbI_2 + HI), $HPbI_3$ precursor layers show relatively similar and slightly dark yellow, while the ($PbI_2 + NH_4I$) precursor layer shows bright yellow. When the precursor layers were exposed to MA gas, they were rapidly transformed into colorless liquid in about several seconds because of the strong coordination with MA. Once removed from the MA gas atmosphere to the ambient air atmosphere, all samples darkened immediately, meaning the rapid release of excess MA gas and the prompt formation of perovskite crystals. After post-heating at 100 °C for 5 min, the four samples exhibited distinctly different colors, as displayed in Fig. 1a_3–d_3. The PbI_2-processed sample shows light brown, while other precursor-processed samples are dark brown. The difference in color implies different composition or crystallization of the four perovskite layers.

For composition evaluation, XRD patterns of the different precursor layers and perovskite layers were recorded. Fig. 2a_1–d_1 are the XRD patterns of the precursor layers, while the XRD patterns of the corresponding perovskite layers are present in Fig. 2a_2–d_2. In addition to the diffraction peaks of the FTO/TiO_2 substrate, the XRD pattern of the PbI_2-processed precursor layer only shows the diffraction peaks of PbI_2, suggesting a pure PbI_2 layer. For the (PbI_2 + HI)-processed precursor layer, no diffraction peak related to PbI_2 is detected, but some unknown and weak diffraction peaks appear, suggesting the formation of a new component with low crystallinity. According to the composition of the precursor solution, the new component may be related to the formation of some intermediate phases, such as $HI{\cdot}\ xPbI_2$, $H_2O{\cdot}HI{\cdot}PbI_2$, $H_2O{\cdot}PbI_2$, etc. For the $HPbI_3$-processed precursor layer, some intense diffraction peaks at 11.5°,15.8°,20.1°and 25.8° are observed, which could be easily indexed to the (1 0 0), (1 0 1), (1 1 0) and (2 0 1) planes of $HPbI_3$ (Long et al., 2016). Therefore, the $HPbI_3$-processed precursor layer is mainly composed of hexagonal $HPbI_3$. All the diffraction peaks on the XRD pattern of the ($PbI_2 + NH_4I$)-processed precursor layer are fully consistent with the simulated diffraction peaks of NH_4PbI_3, attesting a pure NH_4PbI_3 precursor layer.

After MA gas treatment, all perovskite layers exhibit diffraction peaks at 14.1° and 28.4°, which could be indexed to the (1 1 0) and (2 2 0) planes of $MAPbI_3$. However, the diffraction peak at 12.6° is still strong for the PbI_2-processed perovskite layer, suggesting that the reaction between PbI_2 and MA gas is weak and only a few $MAPbI_3$ crystals are formed. For the (PbI_2 + HI)-, $HPbI_3$- and ($PbI_2 + NH_4I$)-processed perovskite layers, the diffraction peaks become much stronger, symbolizing a higher crystallinity. The weak peak at 29.4° in Fig. 2a_2–d_2 corresponds to PbO. Since the MA gas treatment was carried out in ambient air atmosphere, the H_2O in air would involve in the $MAPbI_3$ formation according to the reaction: $3PbI_2 + 2MA + H_2O \rightarrow 2MAPbI_3 + PbO$ (Raga et al., 2016). Almost no diffraction peak of PbI_2 is detected, indicating a complete transformation. Among all perovskite layers, the ($PbI_2 + NH_4I$)-processed one shows the most intense diffraction peaks, demonstrating the highest crystallinity.

The variation in the crystallinity and composition of the perovskite layers should be stemmed from the diversity in the reaction mechanism for different precursors. The pure PbI_2 may react with the MA through the reaction of $PbI_2 + xMA \rightarrow PbI_2{\cdot}\ xMA$ in MA atmosphere (Long et al., 2017). Once removed out, most of the liquid $PbI_2{\cdot}\ xMA$ would be decomposed to solid PbI_2 and MA gas, and only a small part of them could react with moisture or polar solvent vapor to form perovskite crystals: $PbI_2{\cdot}xMA + H_2O \rightarrow MAPbI_3 + PbO$ (Raga et al., 2017; Long et al., 2016). Two reasons may account for the low conversion rate of PbI_2 precursor. Firstly, H^+ plays an important role in the formation of MA^+ (Pang et al., 2016b) and almost no H^+ are present for inducing this reaction for the PbI_2 precursor. In addition, new Pb—I bonds are needed to form PbI_3^- to react with MA^+ to generate $MAPbI_3$. However, no extra I^- could be adopted for this reaction. For the (PbI_2 + HI)-processed precursor layer, H^+/I^- and/or H-I reactants are present. During MA gas exposure, MA^+ would be generated by the acid-base reaction between H^+ and MA and extra I^- would combine with PbI_2 to form PbI_3^-. As a result, $MAPbI_3$ would be easily formed in MA gas atmosphere, which would then transform into a colorless liquid intermediate phase of $MAPbI_3{\cdot}xMA$ with the uptake of excess MA molecules. After being taken out from the MA atmosphere, excess MA molecules release, and $MAPbI_3$ re-nucleates and crystallizes into perovskite crystals. Accordingly, the pure $HPbI_3$ precursor layer also meets the requirements to be converted to $MAPbI_3$ in MA gas atmosphere. Furthermore, compared with the (PbI_2 + HI)-processed precursor, no H_2O molecules that are detrimental to $MAPbI_3$ were present during the conversion process. Consequently, the perovskite layer with the higher crystallinity and quality is obtained. For the ($PbI_2 + NH_4I$) precursor layer, the uptake of MA molecules would result in the reaction of $NH_4PbI_3 + MA \rightarrow MAPbI_3 + NH3$ (Raga et al., 2017; Zong et al., 2016). The release of by-product NH_3 molecules resists the insertion of MA molecules so that the film firstly became dark brown and then turned into colorless slowly.