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Efficient Perovskite Solar Cell Fabricated Using an Aqueous Lead Nitrate Precursor

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A novel, aqueous precursor system (Pb(NO₃)₂ + water) is developed to replace conventional (PbI₂ + DMF) for fabricating methylammonium lead iodide (MAPbI₃) perovskite solar cells (PSC). When the morphology and surface coverage of the Pb(NO₃)₂ film was controlled during coating, a power conversion efficiency of 12.58% under a standard condition (AM1.5, 100 mW/cm²) was achieved for the PSC.

Inorganic-organic lead halide perovskite crystals possess a superior light absorption capability and tuneable bandgap, rendering them promising for use in organic semiconductors, photo-detectors, and photovoltaics. The goal of using methylammonium lead iodide perovskite (MAPbI₃) as a light harvester for organic photovoltaics began in 2009, when Miyasaka et al. fabricated the first MAPbI₃ (X = Br or I)-sensitized solar cells by using a liquid electrolyte. However, liquid electrolytes are corrosive against perovskite crystals and were replaced by solid-state hole conductors, which improve power conversion efficiency (PCE) and device stability. To date, a certified PCE of perovskite solar cells (PSCs) exceeding 20% has been achieved.

One of the advantages of PSCs is that although their architecture is versatile, they can be fabricated using cost-effective and scalable solution processes. In general, MAPbI₃ crystals, the product of a lead-containing precursor and methylammonium iodide (MAI), are formed through one-step or sequential deposition, depending on whether the lead source and MAI are deposited onto the substrate once or sequentially. MAPbI₃ is the most explored perovskite material, and various lead-containing precursors such as lead iodide (Pbl₂), lead chloride, lead acetate, hydroiodized lead iodide, lead acetylacetone, and lead thiocyanate have also been studied. Pbl₂ is the basic material used in preparing MAPbI₃, because it contains lead as well as iodide. Although the photovoltaic performance yielded by different lead precursors varies, almost all studies have used high polarity, aprotic solvents such as dimethylformamide (DMF) because of the solubility.

Concerns regarding the toxicity of PSCs have been addressed recently; organo-lead compounds are severely harmful to the human body and the environment. Therefore, research on creating lead-free PSCs is intensive. While most debate addresses on the hazard of organo-lead in perovskite crystals, in this paper, we propose concerns regarding the processing solvent used during perovskite deposition. Compared with lead perovskite, the pathology of which is uncertain, DMF is a toxicant and has been linked to liver disease clinically. Herein, we report our first attempt to fabricate highly efficient PSCs by using a water-based lead-precursor, lead nitrate (Pb(NO₃)₂), and sequential deposition. The Pb(NO₃)₂ was combined with water, and the surface morphology and formation of the perovskite structure were carefully scrutinised using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The Pb(NO₃)₂/water system is an alternative system that can be used in PSCs without the need for toxic solvents. During current optimisation, a PCE of 12.58% was achieved under standard test condition (AM1.5, 100 mW/cm²).

Figure 1 shows a schematic diagram of the device architecture and the process for fabricating perovskite layers in the Pb(NO₃)₂/water system. The device architecture (Fig. 1a) features a bilayer structure comprising a blocking (BL) TiO₂ layer and a mesoporous TiO₂ scaffold, which benefits charge collection and hysteresis minimisation. The perovskite layer was prepared using sequential deposition, primarily according to the process described in a published report; however, the Pbl₂/DMF precursor solution was replaced by an aqueous Pb(NO₃)₂ solution. The process we used (Fig. 1b) involves additional UV-ozone pre-treatment on the mesoporous TiO₂-containing substrate before Pb(NO₃)₂ spin-coating to enhance wettability between the mesoporous TiO₂ and hydrophilic Pb(NO₃)₂. Fig. 1c shows an XRD analysis of the resulting perovskite film. The conversion of Pb(NO₃)₂ to MAPbI₃ by using DMF as processing solvent has been confirmed in previous studies, and, our results further reveal that perovskite crystals can be formed in an aqueous Pb(NO₃)₂ solution. According to Fig. 1c, diffraction peak at 2θ = 14.2°, 28.5°, and 31.9° correspond to the (110), (220), and

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* Electronic Supplementary Information (ESI) available: Details information about the synthesis of MAI, device fabrication, characterization and other experimental data mentioned in main text. See DOI: 10.1039/x0xx000000x
(312) lattice planes of the perovskite, respectively. The diffraction peak at 12.7°, which is commonly found in a PbI₂/DMF system and represents the incomplete conversion of PbI₂ to MAPbI₃, becomes extremely weak in the Pb(NO₃)₂/water system, indicating the inherent advantage of a higher conversion of lead precursor and a purer perovskite crystal in the Pb(NO₃)₂/water system. Another feature apparent in the XRD results for the Pb(NO₃)₂/water system is that the peak intensity at 31.9° is relatively higher than that in the PbI₂/DMF system. This higher intensity may be attributed to the preferred orientation of crystal growth, which was altered in the Pb(NO₃)₂/water system. However, how it affects the photovoltaic property of perovskite crystal remains unknown and warrants investigation.

Notably, during the preparation of the perovskite layer in a Pb(NO₃)₂/water system, care must be taken in the spin-coating step. The morphology of Pb(NO₃)₂ strongly depends on the wettability between the hydrophilic Pb(NO₃)₂ and the TiO₂ scaffold. Figure 2 shows the SEM topographies of the samples after aqueous Pb(NO₃)₂ was spin-coated onto a TiO₂ scaffold. Without treatment on the surface before spin-coating, the resultant film has an extremely coarse, uneven morphology. Apparent in Fig. 2a, before MAI incubation, diffraction peaks of pristine Pb(NO₃)₂ were found at 2θ = 19.6° and 22.7°. After a fluoride-doped tin oxide (FTO)/TiO₂/Pb(NO₃)₂ substrate was immersed in an MAI solution for 100 seconds (red line), the XRD features of the Pb(NO₃)₂ vanished and a new signal at 2θ = 12.7° indicated PbI₂ formation. When the incubation time increased, the diffraction peaks at 2θ = 12.7° gradually decreased and new diffraction peak at 2θ = 14.2° gradually increased, indicating the formation of the MAPbI₃ phase.

On the basis of XRD observation, we propose that the formation of MAPbI₃ from Pb(NO₃)₂ involves a two-step reaction:

\[
Pb(NO₃)₂ + 2MAI \rightarrow PbI₂ + 2MANO₃ \tag{1}
\]

\[
PbI₂ + MAI \rightarrow MAPbI₃ \tag{2}
\]

The first step is the formation of PbI₂, during which time Pb(NO₃)₂ is exposed to the MAI solution (reaction 1). Indicated as a red line of Fig. 3a, this reaction was rapidly completed within 100 seconds, and the characteristic peaks of pristine Pb(NO₃)₂ disappeared entirely, leaving only the characteristic peaks of PbI₂. Interestingly, no characteristic peaks representing MAPbI₃ are apparent on the red line, indicating that MAPbI₃ cannot be formed directly from Pb(NO₃)₂. In contrast to reaction 1, reaction 2, the transformation of PbI₂ to MAPbI₃, is much slower. Compared with reaction 1, which occurs within 100 seconds, reaction 2 requires approximately 700 seconds to entirely consume the PbI₂ formed from reaction 1. Compared with in a conventional PbI₂/DMF system, the...
propagation and crystal growth of MAPbI$_3$ can be completed within few seconds$^{12}$. Our results suggest that reaction 1 plays an important role to the kinetics of reaction 2, and the consumption of MAI in reaction 1 may account for this; however, such consumption requires further investigation.

Despite the slow rate of MAPbI$_3$ formation in the Pb(NO$_3$)$_2$/water system, the XRD results revealed a noticeable feature that may benefit the photovoltaic property: the amount of unconverted Pb$_2$I$_4$ was minimised. To qualitatively express the conversion of MAPbI$_3$, we define the conversion of MAPbI$_3$ ($C_{\text{MAPbI}_3}$) in reaction 2 as

$$C_{\text{MAPbI}_3} \equiv \frac{I_{127} + I_{142}}{I_{127}}$$

where $I$ is the intensity of the defined diffraction peak in Fig. 3a. The correlation between $C_{\text{MAPbI}_3}$ and the MAI incubation time is showed in Fig. 3b. When the MAI incubation time increased, $C_{\text{MAPbI}_3}$ increased to 69.7% until 500 seconds, approximately the same percentage as that when MAPbI$_3$ was fabricated using the PbI$_2$/DMF system and 100 seconds of MAI incubation (blue dot, Fig. 3c). As mentioned previously and in published reports,$^{10}$ the conversion of MAPbI$_3$ by using the PbI$_2$/DMF system is not complete because of an inevitable pristine PbI$_2$ residue. Interestingly, in the Pb(NO$_3$)$_2$/water system, the $C_{\text{MAPbI}_3}$ increased consistently and reached a plateau higher than 90% after 700 seconds of MAI incubation. To obtain deeper insights into MAPbI$_3$ crystal growth, the topographies of the XRD curves in Fig. 3a were scrutinised using SEM; Fig. 3c provides a summary. In the figure, the surface coverage of TiO$_2$ is imperfect owing to the islandish deposition of Pb(NO$_3$)$_2$ mentioned previously. A careful inspection of these images reveals that different crystal appearances during particular MAI incubation periods can be identified: sheet-like crystals in the early stage (100 seconds), various shapes of crystals containing irregular grains and thin rods in the intermediate stage (300–500 seconds), and thick rods and cuboid crystals in the final stage (after 700 seconds). According to XRD analysis, the formation of MAPbI$_3$ from Pb(NO$_3$)$_2$ can be classified into three stages: Pb$_2$I$_4$, MAPbI$_3$-rich, and MAPbI$_3$-dominated phases. Integrating the information obtained from the XRD and SEM analyses, we speculate that the mechanism is as the follows: First, the Pb(NO$_3$)$_2$ reacts with MAI rapidly in an MAI solution and forms sheet-like PbI$_2$ crystals through ion displacement. Second, preferential nucleation of the MAPbI$_3$ at a particular facet results in lateral growth of crystals, changing the characteristic XRD pattern. Zoom-in images at 100 seconds and 200 seconds of the MAI incubation samples are provided in Figure S2, in which dramatic changes in crystal shapes, from sheet-like to irregular shapes, are apparent, verifying our speculation. Further crystal growth and an increasing volume during MAPbI$_3$ formation forces Pb$_2$I$_4$/MAPbI$_3$ cocktails to merge, causing the irregular shape in the MAPbI$_3$-rich stage. Finally, large MAPbI$_3$ crystals tend to form cuboids or thick rods because of the long incubation duration.$^{31, 32}$

Figure 4 shows the photovoltaic performance of PSCs fabricated using Pb(NO$_3$)$_2$/water and PbI$_2$/DMF precursor systems and the corresponding top-view images of MAPbI$_3$-capped devices. In Fig. 4a, the current–voltage (J–V) curves of the optimally performing devices and their photovoltaic parameters are depicted in the table. The curves plotted in Fig. 4a are the averaged results of two scans from both sides. According to Fig. 4a, for the Pb(NO$_3$)$_2$/water system, the short-circuit photocurrent density ($J_{\text{SC}}$), open-circuit voltage ($V_{\text{OC}}$), and fill factor (FF) values derived from J–V curve are 21.81 mA/cm$^2$, 0.94 V, and 0.61 respectively, causing a PCE of 12.58% under one sun illumination. By comparison, PbI$_2$/DMF system yields a PCE of 14.38%, with a $J_{\text{SC}}$ of 21.99 mA/cm$^2$, a $V_{\text{OC}}$ of 1.04 V and an FF of 0.63. Although the PCE deviates by 1.8% when the aqueous Pb(NO$_3$)$_2$ precursor is used, Fig. 4a indicates that the $J_{\text{SC}}$ of the two devices is almost the same, revealing that the quality of the MAPbI$_3$ is nearly identical; the major difference in photovoltaic parameters of these two devices ($V_{\text{OC}}$ and FF) is attributable to the morphology of the MAPbI$_3$ cap. Shown in Fig. 4b, the MAPbI$_3$ crystals appear as a capping layer that fully covers the TiO$_2$ scaffold in the PbI$_2$/DMF system, whereas the MAPbI$_3$ crystals fabricated using the Pb(NO$_3$)$_2$/water system failed to form a continuous capping film; thus, areas bare of TiO$_2$ are evident in Fig. 4c. The defect in the MAPbI$_3$ capping layer in the Pb(NO$_3$)$_2$/water system originates from the islandish deposition caused by spin-coating Pb(NO$_3$)$_2$, reflecting that the current film technology involving aqueous Pb(NO$_3$)$_2$ is far from perfect.
Nevertheless, our results confirm that using an aqueous lead source instead of a toxic DMF solvent is a viable method for fabricating high-purity perovskite crystals and highly efficient PSCs featuring a PCE exceeding two digits.

In summary, we developed a novel precursor combination for fabricating highly efficient PSCs by using an aqueous Pb(NO$_3$)$_2$ solution and created water-processed PSCs with a 12.58% PCE under standard conditions (AM1.5, 100 mW/cm$^2$). To the best of our knowledge, this is the first report of using water as processing solvent for PSCs. Eliminating the use of polar, toxic processing solvents such as DMF enables the feasibility of green production for PSCs. Moreover, we determined that the formation of MAPbI$_3$ from Pb(NO$_3$)$_2$ is a two-step reaction, proposing a possible mechanism involving the rapid formation of PbI$_2$ intermediates and the slow reaction of PbI$_2$ and MAI to form MAPbI$_3$. The inherent advantages of this process can be realised; for example, stoichiometrically controlling multi-halide perovskite becomes easy because the iodide no longer exists in the precursor, but rather exists in the MAI solution. The wettability between the substrate and Pb(NO$_3$)$_2$ during spin-coating is another concern; our UV-ozone treatment is effective but imperfect and requires improvement to enable a full-coverage coating. This study reveals that fabricating highly efficient PSCs by using a cost-effective, environmentally friendly process is promising.

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Notes and references

2. J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal and S. I. Seok, Nano letters, 2013, 13, 1764-1769.