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The influence of DMSO and ether via fast-dipping treatment for a perovskite solar cell

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ABSTRACT

Preparing dense organic-inorganic hybrid perovskite film is hindered by the extremely low solubility of lead(II) iodide (PbI_2) at one-step coating process using one-solution (PbI_2 + CH_3NH_3I + DMF). Thus, dimethyl sulfoxide (DMSO) has been widely used to enhance the solubility through the formation of adducts. However, the required mixture of DMSO and DMF cannot be simultaneously evaporated at low temperatures, owing to the different boiling points, which are influenced by the surface morphology. Consequently, this also affects the solar energy conversion efficiency of the perovskite solar cells. In this study, we develop a new approach for controlling the evaporation of DMF and DMSO by dip-coating ether on the top of the prepared thin film composed of PbI_2, methylammonium iodide (MAI), DMF, and DMSO. Interestingly, it reveals that ether acted as an agent for simultaneous evaporation at similar temperatures, which then allows it to control surface morphology, and achieve dense perovskite. The fabricated inverted-perovskite PbI_2 thin film solar cell shows that the efficiency reached up to 16.3% with high reproducibility. The ether-dipping post-treatment serves as a promising means for enhancing the efficiency of perovskite solar cells.

1. Introduction

Solar energy has received much attention as a renewable energy source, because of the depletion of fossil fuels. There are many studies about solar cells that convert light energy into electrical energy. In recent years, interest has increased in solar cells using a perovskite structure as a photoactive layer. The perovskite structure refers to a substance having a chemical formula, ABX_3 [1–3]. Following the first report of perovskite solar cell in 2009, substitutes such as organic–inorganic hybrid perovskite, such as methylammonium lead halide ($CH_3NH_3PbX_3$ ($MAPbX_3$)),replaced the expensive Si-based photovoltaic devices [3]. There has been an explosion of interest and several studies on Pb halide-based organic-inorganic hybrid cells, since a report appeared in 2012 that described the efficiency of perovskite solar cells as being ≥ 9% [4–8].

Because so many studies have been conducted on perovskite solar cells over the last few years, there is now increased interest in how to make perovskite layers. The perovskite formation method is generally divided into a one-step process or a two-step process, depending on the number of coating procedures. A one-step process is currently being investigated in order to lower the cost of the solar cell fabrication process [9,10]. Another big issue is how to improve the quality of film formation in order to get high-efficiency solar cells. Morphological control is very important in order to achieve dense and high-quality perovskite films e.g., a thorough adding treatment process [11–16], using heterogeneous materials [17–22] or changing coating conditions [8,23–30].

The above-mentioned two issues must be solved at the same time in order to make a high–efficiency solar cell through a one-step method.

First, in order to use the one-step method, it is necessary to solve the problem of the relative poor solubility of PbI_2 compared to methylammonium iodide (MAI). One group of researchers attempted the solvent method using MAI and PbI_2 in DMF and γ–butyrolactone as the mixing agents. The purpose was to increase the solubility of PbI_2 and apply it to a one-step process using one solution [9,13]. Another group dissolved the MAI and PbI_2 in a solution of dimethylacetamide (DMAC) and N–methyl–2–pyrrolidone at a ratio of (1:5) [31]. Several groups have reported on a chlorobenzene (CB) –based solvent–assisted process [11,12]. Fabrication of high-quality perovskite films have been reported using these methods. However, γ–butyrolactone, DMAC and CB are also known to be toxic to humans. Therefore, there is an urgent demand to develop new methods to make a dense perovskite solar cell. One alternative, DMSO, has recently been used in studies. It is added in the solution for morphological control of the perovskite layer in a

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TiO_2–based device [15]. However, when compared to conventional structures, few studies have been conducted on inverted solar cells.

Various coating or treatment methods are now being used to fabricate high-quality perovskite films. Researchers have typically used commonly available deposition apparatuses under high-vacuum conditions to deposit perovskite films e.g., a thermal evaporator or technology incorporating chemical vapor deposition [8,27,28]. There are enormous financial costs associated with these methods. Dropping diethyl ether method has been reported as a replacement for toluene-drop treatment during the spin-coating step [9]. However, with the exception of the use of a special device, the method of dropping ether during spin coating may not be reproducible. It is also difficult to use a general micro-pipette tip, since ether has a low viscosity of 0.224 cP.

Herein, we studied the fabrication of a inverted perovskite solar cell using poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) and [6,6]-phenyl-C61-butyric acid (PCBM) as transport layers. The perovskite solution was dissolved in mixture comprised of DMSO and DMF solvents. An ether dipping process was conducted at the same time to achieve spin-coating over a short period of time. This experiment is aimed to form the dense perovskite thin film by controlling the crystallization speed.

2. Experimental

2.1. Materials

PEDOT:PSS (PH1000) was purchased from Heraeus Clevios™, Germany. Methylamine solution (CH_3NH_2, 40 wt% in H_2O, 426466–1L), lead(II) iodide (PbI_2, 99%, 211168–50G), dimethyl sulfoxide (DMSO, $(CH_3)_2SO$, ≥ 99.5%, (GC), plant cell culture tested, D4540–1L), N-dimethylformamide (DMF, $HCON(CH_3)_2$, ≥ 99%, for molecular biology, D4551–500ML), 2-propanol (IPA, $(CH_3)_2CHOH$, ≥ 99.5%, for molecular biology, bioReagent, I9516–500ML) chlorobenzene (CB, C_6H_5Cl, ≥ 99.5%, ACS reagent, 319996–1L), hydriodic acid (HI, 99.95%, 57 wt% in H_2O, distilled stabilized, 210021–50ML), bathocuproine (BCP, $C_{26}H_{20}N_2$, 96%, 140910–1G) was purchased from Sigma Aldrich (St. Louis, Missouri, USA). Ether ($C_4H_{10}O$, diethyl ether, 99.0%, GC grad, E0285) was purchased from SAMCHUN Chemical, Korea. Phenyl C_{61} butyric acid methyl ester (PCBM), $C_{72}H_{14}O_2$, 99.5% by high-performance liquid chromatography (HPLC), < 0.5% other fullerenes, nano-cPCBM-BF (60) was purchased from ano-C Inc (Westwood, MA, USA). Silver (Ag, EAG0CE0001) was purchased from TAEWON SCIENTIFIC CO., LTD, KOREA

2.2. Synthesis of MAI

A mixture of HI and $CH_3NH_2$was combined in a round-bottom flask (250 mL), placed in an ice bath, and constantly stirred for 3 h. The residual solvent was removed using a rotary evaporator. MAI was then washed several times with diethyl ether. The final product, a powder, was then dried under vacuum for overnight.

2.3. Solar cell fabrication

The substrate was rinsed with de–ionized water and subsequently cleaned for 10 min at a time with successive solutions of acetone, ethanol, and isopropyl alcohol in order to remove organic contaminants on the ITO–glass substrate. The PEDOT:PSS films were prepared by the spin–coating method at 4000 rpm for 30 s. Then the PEDOT:PSS films were dried at 160 °C for 30 min on a hot plate (HSD180, MISUNG SCIENCTIFIC Co.).

The active layer was deposited by as pin–coating process at 4000 rpm for 10 s using 50 wt% mixing solutions with MAI, PbI_2, and DMSO in 1:1:1 molar ratios. To understand the role of DMSO, a 1:1 molar ratio solution with MAI and PbI_2 was prepared and deposited under the same conditions. After spin–coating process, these films were

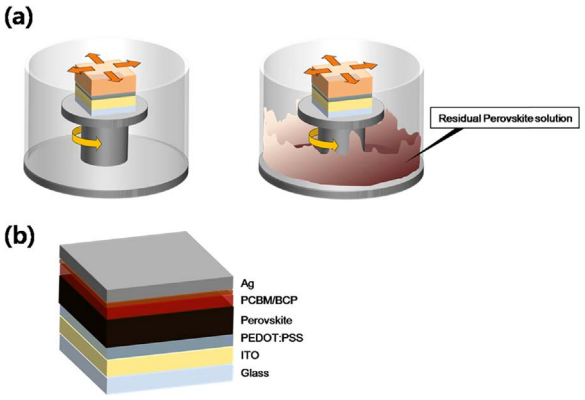

Fig. 1. Schematic image of (a) spin-coating, residual solution after process. And (b) schematic diagram of the fabricated solar cell.

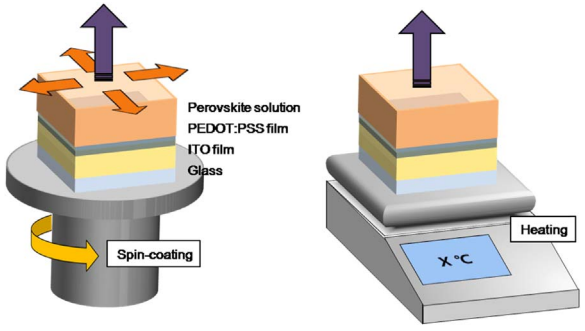

Fig. 2. Schematic image of spin-coating and heating process. The upward arrows on the top of the sample indicate the evaporation of the solvent and the orange arrow in the parallel direction indicates the removal of the solution by centrifugal force. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

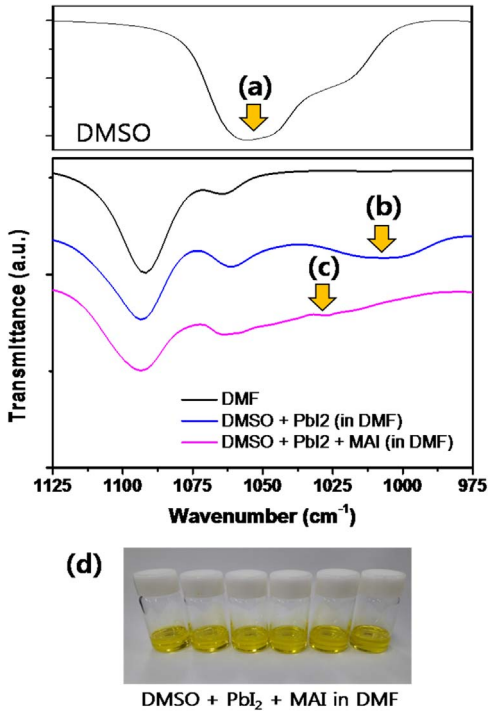

Fig. 3. The FT-IR spectra of pure DMSO, (a) pure DMF, (b) DMSO–PbI2 complex (in DMF), and (c) DMSO–PbI2–MAI complex (in DMF). And (d) a camera image of perovskite one solution (DMSO, PbI2, and MAI in DMF).