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Solution-processed nickel oxide hole transport layer for highly efficient perovskite-based photovoltaics

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ABSTRACT

Solution processed NiO_x is one of the promising hole transport layer (HTL) for planar perovskite solar cells, which can replace hygroscopic poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) HTL. In this study, we investigated effects of ethylenediamine (EDA) additive in NiO_x precursor solution (nickel nitrate hexahydrate dissolved in ethyleneglycol) on optoelectronic and surface morphological properties of resultant solution processed NiO_x films. By varying EDA content (0–10.0 v/v %) in the precursor, we could find out that adequate EDA additive (~5.0%) provide much reduced electrical resistivity and enhanced optical transmission compared with control NiO_x film (No EDA) by suppressing formation of byproducts (i.e. nickel hydroxide). In addition, AFM surface topography showed much compact and dense deposition of NiO_x film on ITO electrode. This contributed to improve charge transport properties and suppress charge recombination loss at ITO/perovskite interface, which provided strong enhancement in fill factor from 0.599 to 0.714 in the perovskite solar cells. As a result, a power conversion efficiency (PCE) was strongly increased from 13.9 (No EDA) to 16.7% (EDA 5.0%). This also outperformed the performance (14.3%) of device using PEDOT: PSS, which indicates that the adequate control of EDA additive for NiO_x HTL could offer much promising photovoltaic performance.

1. Introduction

Organolead halide perovskite solar cells have been received considerable attention due to its high power conversion efficiency (PCE) over 22% [1], low materials costs, and simple fabrication using solution processing [2]. Strong optoelectronic properties of perovskites such as strong absorption coefficient, long diffusion lengths and good mobility of charge carriers are fundamentals for achieving such impressive photovoltaic performances [3–5]. Bandgap tuning with varying composition of perovskites can also provide construction of tandem architecture under proper combination of different bandgaps [6,7]. Besides of the promising perovskite light absorber, hole transport layer (HTL) and electron transport layer (ETL) have been widely studied for efficient charge extraction/collection [6]. Recently, organometallic precursors have been widely employed to form metal-oxide thin film instead of organic charge transport layers due to their low long-term stability under oxidation and/or relatively high material costs [8]. In case of conventional n-i-p structure of fluorine-doped SnO_2 (FTO)/ETL/perovskite/HTL/rear metal, TiO_2 [1,9] or ZnO [10] have been representatively used as ETL, however, a high sintering process of TiO_2 over 450 °C limits flexible application of the perovskites. Solution-processed ZnO ETL also has some issues of reaction between methylammonium iodide (MAI) and ZnO, so variation of coating technology is needed [10]. As for inverted planar architecture of indium-tin-oxide (ITO)/HTL/perovskite/ETL/rear metal, on the other hand, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS, PVP AI 4083) as a hole transport layer (HTL) has been used its benefits of low temperature processing and simple fabrication [11]. In spite of good hole collecting properties of the PEDOT: PSS, hygroscopic nature could limit long-term stability of organic/perovskite solar cells [12]. Instead, various metal oxides such as NiO_x [8], CuO_x [13], and etc. have been developed as HTL [14,15]. The NiO_x showed satisfactory hole-collecting properties with deeper valence band (− 5.3 – − 5.4 eV) than PEDOT: PSS which can increase open circuit voltage (V_{oc}) of the solar cells [6].

There have been various fabrication techniques using different nickel precursors and solvents to form NiO_x thin films such as nickel formate dihydrate with ethylenediamine (EDA) [16], nickel acetate tetrahydrate complexed with methanolamine [17], nickel nitrate hexahydrate with MEA (monoethanolamine) [18], nickel nitrate hexahydrate with ethyleneglycol and EDA [8]. We have also been employing nickel nitrate hexahydrate with ethyleneglycol solvent and EDA additive to form the NiO_x thin film as HTLs for inverted planar architecture of perovskite solar cells. For high performance of solar cells,

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highly conductivity, wide-bandgap, good matching of valence band level with perovskites, and simple processing (under low temperature) are required characteristics of the NiO_x HTL, which depends on the fabrication of solution processing with different solvents/additives. On the other hand, effects of the EDA additive concentration on properties of formed NiO_x thin films and thus their application on perovskite solar cells have been scarcely reported to date. The solvent/additive analyses on formation of resultant films are required to obtain high quality metal oxide HTL. Thus, in this work, we varied relative volume ratio of EDA additive (0–10% v/v) in precursor composition (nickel nitrate hexahydrate dissolved with ethyleneglycol solvent). From the fabricated NiO_x thin films, optoelectronic and surface morphological analyses have been made to characterize them. With proper EDA partial concentration of ~5%, highly transparent and low resistive NiO_x films were obtained. Also, compact and dense morphology was also found, which is preferred for low recombination loss for photovoltaic device operation [19]. As a result, this NiO_x HTL contributed to achieve an impressive PCE about 16.7%, whereas the best performing devices using conventional PEDOT: PSS and NiO_x without EDA additive showed 14.3% and 13.9%, respectively. This precursor optimization using adequate additive for NiO_x HTL can be strongly beneficial to achieve high performance inverted planar perovskite photovoltaics with very simple solution processing.

2. Experimental detail

2.1. Information of materials

MAI (Methyl ammonium iodide, 99.99%), PbI_2 (99.9985%) were purchased and used as is to make precursors for $MAPbI_3$ perovskites. DMF (Dimethylformamide, 99.5%), DMSO (Dimethyl sulfoxide, 99.8%), CBZ (chlorobenzene, mono, > 99.5%) were employed as main solvents and/or anti-solvents. For charge transport materials, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS, PVP AI 4083) as a hole transport layer (HTL) and Phenyl-C61-butyric acid methyl ester (PCBM, 99.5%, Nano-C) as an electron transport layer (ETL) were used as is. In addition, NiO_x precursor solution was made using $Ni(NO_3)_2{\cdot}6H_2O$ (99.999%), ethyleneglycol (99.5%), and ethylenediamine (EDA, 99.0%).

2.2. Preparation of NiO_x thin films

For characterization of the solution processed NiO_x HTL, it was coated on bare glass or ITO substrates. First, NiO_x precursor solutions with various EDA additive concentration (0, 2.5, 5.0, 6.7, 7.5, 10.0 v/v %) were made by dissolving nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) of 0.291 g in ethyleneglycol of 1 mL. The solutions were stirred at room temperature for 12 h. The image of resultant solutions is shown in Fig. 1. The NiO_x precursor solutions with various EDA concentration (0–10.0%) were coated onto each substrate at 4000 rpm for 90 s and annealed at 300 °C for 60 min in air-ambient.

2.3. Device fabrication

ITO glass substrates (15 $\Omega{\cdot}sq^{-1}$) were cleaned with a sequential step of acetone, methyl alcohol, and isopropyl alcohol for 10 min, respectively. After drying them in an oven, UV-ozone treatment for hydrophilic surfaces was made for 20 min. Then PEDOT: PSS (PVP AI 4083) solution was spin-casted on the substrates at 4000 rpm for 50 s and annealed at 140 °C in air-ambient. Regarding perovskite precursor, $MAPbI_3$ (50 wt%) perovskite solution was made by dissolving MAI (0.286 g) and PbI_2 (0.830 g) 1 mL DMF with DMSO (128 μL), and stirred at 65 °C for 12 h. Afterward, $MAPbI_3$ perovskite precursors (filtered with a 0.45 μm PVDF filter) were spin-casted on the PEDOT: PSS or NiO_x HTLs in a glovebox. And then, the $PC_{61}BM$ solution was spin-coated onto the perovskite films at 400 rpm for 1 s and 1500 rpm at 35 s

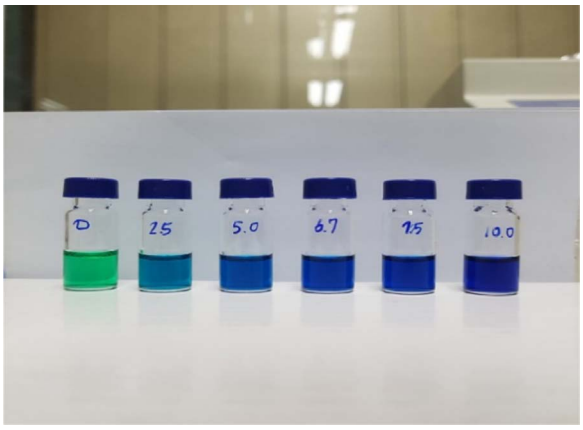

Fig. 1. Fabricated NiO_x precursor solutions with different ethylenediamine (EDA) concentration from 0% to 10.0% (v/v).

in the glovebox too. Finally, silver electrode was thermally-evaporated under high vacuum through a shadow mask. The active area of solar cells was 4 mm^2.

2.4. Characterization of films and devices

Optical transmittance spectra of the various HTLs were characterized by ultraviolet-visible (UV–Vis) spectrophotometry (UV-2700; Shimadzu). Fourier transform infrared (FT-IR) measurement was performed to analyze film components by using the equipment (Vertex 80 v; Bruker) with a detector detector (mercury-cadmium-telluride: MCT) and a beam-splitter (KBr). The FT-IR was measured with scanning 128 times under a resolution of 2 cm^{-1}. The film thicknesses were measured by a surface profiler (D-100; KLA Tencor). Surface morphologies of the various NiO_x HTLs were analyzed by using atomic force microscopy (AFM) (SA-AFM; Proves Inc.). Electrical resistivity of those NiO_x films were estimated by preparing patterned Ag-electrodes on film surfaces, and following current-voltage sweeping was made with using a parameter analyzer. All current density-voltage (J-V) curves of the fabricated perovskite solar cells were measured by a solar simulator (Polaronix K201; McScience) under an AM 1.5 standard condition in air-ambient (100 mW/cm^2, relative humidity = 20–30%, 25 °C).

3. Results and discussion

In this study, perovskite solar cells were constructed based on p-i-n type inverted planar structure. On the ITO-glass, PEDOT: PSS or NiO_x hole collectors were deposited before coating of perovskite light harvester, which means that optical transmission of those HTL is crucial to make light in-coupling into perovskite absorber. Thus, we first characterized optical transmittance of fabricated NiO_x films with various EDA additive concentration (0–10.0%) as well as PEDOT: PSS as HTLs, as shown in Fig. 2. In comparison with the PEDOT: PSS, we could find the pronounced transmission of the NiO_x films regardless of the EDA additive concentration (0–10.0%) in whole spectral wavelengths. This can be attributed to wide bandgap (~3.2–3.6 eV) of the NiO_x compared with that (~2.0–2.2 eV) of PEDOT: PSS [16,20–22]. This indicates that the metal oxide film can further reduce parasitic absorption loss at HTL, which allows for transmission of more incident light into perovskite absorber. It is beneficial to improve short circuit current (J_{sc}) of photovoltaic cells. As for the NiO_x samples with various EDA concentration, the NiO_x films made without EDA additive and made with EDA of 10% showed slight lower transmission compared with films made using EDA additive ratio (2.5–7.5%). This can be elucidated with compositional analyses of the solution processed NiO_x films.

Fig. 3 shows FT-IR absorption spectra of the solution processed NiO_x