All solution processed perovskite solar cells with Ag@Au nanowires as top electrode

CrossMark

Tang Liu, Wenqing Liu, Yuting Zhu, Shengping Wang, Gang Wu, Hongzheng Chen*

State Key Laboratory of Silicon Materials, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

ABSTRACT

In this paper, solution-processed Au-coated Ag nanowires (Ag@Au NWs) was successfully fabricated as top electrode by spray deposition in planar perovskite solar cells (PVSCs) with structure ITO/PTAA:F4-TCNQ/ MAPbI$_3$/PC$_{61}$BM/Ag@Au NWs, which shows favorable bandgap alignment. Sheet resistance of electrode and series resistance of solar cells over time as well as the stability of PVSCs were measured. The results indicate that the Au shell which serves as a physical separation layer sandwiched in between the perovskite/hole transporting layer (HTL) and the halide-reactive silver nanowires (Ag NWs) can significantly enhance the stability of PVSCs. The efficiency of solar cells employing Ag NWs as top electrode decreases rapidly within 10 min while the efficiency of solar cells employing Ag@Au NWs still remains 85% of its original efficiency even after one week in air. The as-fabricated PVSCs exhibit a power conversion efficiency of 11.0% with an open-circuit voltage of 0.99 V, a short-circuit current density of 18.5 mA/cm^2, and a fill factor of 64.3%. This work paves a way for realizing low cost, stable, all solution processable PVSCs.

1. Introduction

Inorganic-organic halide perovskite solar cells (PVSCs) have recently emerged as a promising photovoltaic technology due to their superb power conversion efficiency (PCE) exceeding 22% [1]. Perovskite has shown great opto-electronic properties such as high carrier mobility [2–4], long exciton diffusion length [5–8]. In addition to their high efficiency, the solution processable property makes it promising for low cost industrial mass production. However, vacuum processed top electrode is undesired for manufacturing not only because of energy waste but also incompatibilty with mass production [9–12]. To address this issue, many studies have reported perovskite solar cells based on solution-processed transparent electrode and top electrode [13–15].

Many materials can be viable candidates for the low cost solution processed electrode that have already been widely applied in organic solar cells, such as graphene [16,17], carbon nanotube (CNT) [18,19], silver nanowire [20], poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) [21–23] and so on [24,25]. Wang et al. [26] demonstrated the hole transport layer (HTL) free PVSCs with single-walled CNT/carbon composite as the count electrode. By adding single-walled CNTs into the graphite and carbon black electrode, the charge collection of electrode as well as the chemical stability and hydrophobicity were enhanced. Han et al. [27] also demonstrated

PVSCs based on screen-printable mesoporous graphite/carbon black counter electrode. The variation of the graphite size will induce differences in the filling of PbI$_2$ and CH$_3$NH$_3$PbI$_3$ precursor as well as the sheet resistance of conductive count electrode. In addition to graphite, carbon nanotubes and graphene are also promising candidates for low cost solution processable electrode. Lin et al. [28] reported HTL free PVSCs with cross-stacked super aligned carbon nanotube sheets as top electrode with an efficiency of up to 8.65%. Choi et al. [29] reported highly efficient transparent conductive oxide-free inverted PVSCs using graphene as transparent electrode. By inserting a few nanometer thickness of MoO$_3$ layer between the graphene and PEDOT:PSS, the hydrophilicity of the graphene surface was increased and the work function was elevated. Despite the relatively high sheet resistance (about 500 Ω/square) of graphene, a high efficiency over 17% was achieved.

Among various solution-processable electrode materials [30–35], Ag NWs offer benchmarking opto-electronic properties of about 90% transmittance at 550 nm and less than 20 Ω/square sheet resistance, comparable to that of the commercial transparent conducting oxides (TCO) electrode [36,37]. The use of Ag NWs as top electrode has recently been demonstrated in PVSCs. Jun et al. [38] reported flexible PVSCs based on a titanium metal substrate employing solution-processed Ag NWs as the top electrode. The Ag NWs were deposited on the

---

top of the HTL of spiroMeOTAD by a carefully controlled spray-coating method at moderate temperature. The PCE reached 7.45% under AM 1.5 illumination. Moreover, Ag NWs have been applied as top electrode of semitransparent tandem solar cells [39]. Ag NWs were dissolved in methanol and spray deposited from solution with a pheumatic airbush-type spray nozzle onto flexible polyethylene terephthalate (PET) film at 60 °C. This airbush-type deposition ensures uniformity and repeatability over an arbitrarily large deposition area. However, the silver electrode for PVSCs turns yellow within days of device fabrication, accompanied by a dramatic decrease in PCE when compared to otherwise identical devices using gold electrodes [37]. A likely mechanism was proposed by Lin et al. [40] that the decomposition of $MAPbI_3$ gives rise to iodine containing volatile species, which will migrate to the bottom and top Ag layer to form silver iodide, leading to the yellowing of the silver electrodes within several days storage. The Ag NWs-based devices have also been reported to undergo rather rapid degradation even when stored in a N_2 atmosphere, as the same as the evaporated Ag electrode based devices [41].

To address this issue, an ultrathin transparent Au layer was evaporated beneath the spin-coated Ag NWs forming a composite transparent metallic electrode, where the Au layer serves as a physical separation to avoid the undesired electrode degradation and simultaneously to improve the Ohmic contact [40]. The efficiency of PVSCs with this composite electrode is 7.53% when light illuminates from Ag NWs side. However, the evaporated Au particles nucleated on the perovskite/HTM surface rather sparsely and formed particle-wise isolated metallic islands, which means it can't fully protect Ag NWs from corrosion. Guo et al. [42] also introduced ZnO nanoparticles as physical separation beneath the Ag NWs. However, the work function of ZnO does not well match with Ag NWs, resulting in poor performance in conventional structure PVSCs. Wu et al. [43] encapsulated of silver nanowires network between a monolayer graphene and polymer film as a sandwich structure. The monolayer graphene and the polymer matrix were introduced as inert cover to avoid the metal mesh from oxidation and corrosion. Despite these efforts, the stability issue of PVSCs persists.

In this manuscript, through rational materials design in combination with judicious selection of deposition techniques, we demonstrate for the first time facial solution processed Au-coated Ag NWs (Ag@Au NWs) as top electrode for efficient PVSCs with device structure of ITO/PTAA:F4-TCNQ/MAPbI$_3$/PC$_{61}$BM/Ag@Au NWs. A thin layer of Au was coated outside of Ag NWs from facial solution processing method, which serves as a physical protect layer and ensures chemical stability of Ag NWs. Compared to the particle-wise isolated metallic islands by directly evaporating Au on perovskite [40], fully protected Ag NWs by Au shell can be realized by tuning Au thickness with our method. Due to the excellent chemical stability of Ag@Au NWs, the as-prepared PVSCs showed not only high PCE of 11.0% with high J_{sc} and FF comparable to their counterparts, but also better performance stability. The PVSCs were fabricated from spin coating and spray depositing without thermal evaporation, indicating the promising for all solution processed, low cost and stable PVSCs.

2. Experimental

2.1. Chemicals and materials

Ag NWs solution (diameter = 40 nm, length = 20 μm, 5 mg/ml, isopropanol solution) was purchased from Suzhou ColdStones Technology Co. Ltd. Poly-triarylamine (PTAA, 99.9%), PbI$_2$ (99.9%), CH$_3$NH$_3$I (MAI, 99.5%), [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM), and polyvinylpyrrolidone (PVP, Mw ≈ 55,000, powder) were bought from Sigma-Aldrich. Tetrachloroauric acid (HAuCl$_4$·4H$_2$O) and sodium chloride (NaCl) were bought from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used without further purification.

2.2. Synthesis of Au-coated Ag nanowires

Ag@Au NWs were synthesized via galvanic displacement reaction according to literature [44]. Typically, 1 ml 5 mg/ml Ag NWs was added dropwise into 20 ml saturated NaCl solution with 2 mM PVP while stirring at 500 rpm. The galvanic displacement reaction was carried out using different amounts of saturated NaCl aqueous solution with 1 mM HAuCl$_4$ that was titrated at a rate of 0.5 drops/s into previous prepared Ag NWs solution. The mixture was stirred at 500 rpm for 2 h to finish the reaction. The broken nanowires and excessive PVP were removed by centrifugation. The sediment was washed by water and isopropanol and finally dispersed in isopropanol at a concentration of 10 mg/ml. Different thickness of Au layer was obtained by changing the volume of HAuCl$_4$ solution. The Au-coated Ag NWs were referred as Ag@Au-x, where x is the ratio of Au atom number of added HAuCl$_4$ to Ag atom number of Ag NWs. Here three different Ag@Au NWs were fabricated, named as Ag@Au-0.1, Ag@Au-0.14, and Ag@Au-0.2, respectively.

2.3. Device fabrication

Indium Tin Oxide (ITO) glass (15 mm × 15 mm) was cleaned sequentially by deionized water, detergent, acetone, isopropanol and ethanol in ultrasonic bath for 20 min followed by ultraviolet UV-ozone treatment for 20 min. 0.5 wt% PTAA solution doped with 1 wt% F4-TCNQ was spin-coated on ITO at 3000 rpm and the as-prepared film was thermally annealed at 110 °C for 10 min. The MAPbI$_3$ films were fabricated by solvent-induced fast crystallization. The precursor MAPbI$_3$ solution was prepared by dissolving 1.57 M MAPbI$_3$ in 1 ml DMF and DMSO mixed solvent with a molar ratio of 8.26:1. The precursor solution was stirred at 70 °C overnight and cooled to room temperature before spin-coating on PTAA film at 8000 rpm. During 4–6 s after the spinning starts, the substrate was treated by drop-casting with 0.5 ml diethyl ether. The substrate was then annealed at 100 °C for 20 min. 20 mg/ml PC$_{61}$BM dissolved in chlorobenzene was spin coated on the perovskite film at 1500 rpm. The solar cells fabrication was finished by spray depositing Ag NWs or Ag@Au NWs as top electrode with a cell area of 0.04 cm^2 determined by using a metal mask. By changing depositing times to control the thickness of Ag NWs and Ag@Au NWs films, the sheet resistance of Ag NWs and Ag@Au NWs films can be easily maintained around at 50 Ω/square.

2.4. Characterization and measurement

UV–vis absorption spectra and transmittance spectra were taken on a Shimadzu UV-2450 spectrometer. The transmittance spectra were measured with an integrating sphere. The morphology of the Ag@Au NWs was imaged using a transmission electron microscope (TEM, *JEM-1230*). X-ray diffraction (XRD) patterns were recorded at a scan rate of 5°/min on a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (1.5406 nm). Current–voltage characteristic curves were recorded under AM 1.5 100 mW cm^{-2} simulated sunlight (TaiWan, Enlitech) with a Keithley 236, previously calibrated with a standard Si solar cell. The IPCE spectra were recorded using an incident photo-to-current (IPCE) measurement system (TaiWan, Enlitech), and the light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The sheet resistance of Ag NWs was measured using a four point probe (TH2661, CHANGZHOU TONGHUI ELECTRONIC CO., LTD.). Morphology of the perovskite film and cross section of devices were taken by a field-emission scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the representative TEM images of Ag NWs and the as-fabricated Ag@Au NWs with different Au shell thicknesses. The diameter of the pristine Ag NWs measured from Fig. 1a is about 45 nm.