Solar Energy 171 (2018) 652–657

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Low temperature processed inverted planar perovskite solar cells by r-GO/CuSCN hole-transport bilayer with improved stability

Towhid H. Chowdhury[a,b,c], Md. Akhtaruzzaman[b,*], Md. Emrul Kayesh[a], Ryuji Kaneko[a], Takeshi Noda[a], Jae-Joon Lee[c], Ashraful Islam[a,*]

[a] Photovoltaic Materials Group, Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba 305-0047, Japan
[b] Solar Energy Research Institute, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor Darul Ehsan, Malaysia
[c] Department of Energy & Materials Engineering & Research Center for Photoenergy Harvesting and Conversion Technology, Dongguk University, Seoul 04620, Republic of Korea

ARTICLE INFO

Keywords:
Copper (I) thiocyanate
Hole-transport bilayer
Perovskite solar cell
Reduced graphene oxide
Stability

ABSTRACT

Low temperature processed Perovskite solar cells (PSCs) are popular due to their potential for scalable production. In this work, we report reduced Graphene Oxide (r-GO)/copper (I) thiocyanate (CuSCN) as an efficient bilayer hole transport layer (HTL) for low temperature processed inverted planar PSCs. We have systematically optimized the thickness of CuSCN interlayer at the r-GO/$MAPbI_3$ interface resulting in bilayer HTL structure to enhance the stability and photovoltaic performance of low temperature processed r-GO HTL based PSCs with a standard surface area of 1.02 cm^2. With matched valence band energy level, the r-GO/CuSCN bilayer HTL based PSCs showed high power conversion efficiency of 14.28%, thanks to the improved open circuit voltage (V_{OC}) compared to the only r-GO based PSC. Moreover, enhanced stability has been observed for the r-GO/CuSCN based PSCs which retained over 90% of its initial efficiency after 100 h light soaking measured under continuous AM 1.5 sun illumination.

1. Introduction

PSCs has been identified as the most promising solar technology for energy harvesting due to their potential high efficiency and easy fabrication process (Park et al., 2016; Correa-Baena et al., 2017; Green and Ho-Baillie, 2017; Seok et al., 2018). Since the inception of PSCs, two main structures such as- mesoporous and inverted planar structures have been under intense investigation. Until now, the highest power conversion efficiency (PCE) of 22.7% has been observed with mesoporous PSCs (Green et al., 2018). However, in the mesoporous structure, the fabrication of electron transport layer requires high temperature (500 °C) sintering process, which hinders their potential aspects for commercialization and potential application in flexible electronic devices. In this aspect, low temperature processed PSCs are more anticipated. Inverted planar structured PSCs with their total low temperature fabrication compatibility is steadily attracting considerable attention.

Generally inverted planar PSCs are fabricated with a *p*-type semiconducting material which acts as a hole transport layer (HTL) is deposited on top of the transparent conductive oxide glass followed by perovskite compound as the absorber and *n*-type semiconducting material as the electron transport material (ETM). The first inverted planar PSCs were originated from the concept of organic photovoltaics where, PEDOT:PSS was used as the hole transport material (Jeng et al., 2013). The low temperature processed PSC showed impressive photovoltaic performances but resulted in rapid degradation and induced decomposition of the perovskite absorber due to the acidic behaviour of the PEDOT: PSS (Chen et al., 2015). To address this issue, recently we have reported on low temperature processed stable inverted planar PSCs with NiO_x nanoparticles (Chowdhury et al., 2018). Alternate low temperature processed HTLs such as Cu_2O (Chatterjee and Pal, 2016), CuI (Sun et al., 2016), CuO_x (Yu et al., 2017), CoO_x (Shalan et al., 2016), CuSCN (Zhao et al., 2015; Ye et al., 2015) has been implemented in PSCs and showed promising aspects but failed to provide stable performances. In stability concern, carbon derivatives such as Graphene (Agresti et al., 2016), Graphene Oxide (GO) (Yang et al., 2017; Liu et al., 2014) and reduced Graphene Oxide (r-GO) (Yeo et al., 2015) are popular choice of HTLs in PSCs. With the capability of higher absorption in the near UV region, GO based PSCs can provide long term stable performance in inverted planar PSCs (Yang et al., 2017). However, for

---

* Corresponding authors.
E-mail address: islam.ashraful@nims.go.jp (A. Islam).

https://doi.org/10.1016/j.solener.2018.07.022
Received 24 April 2018; Received in revised form 28 June 2018; Accepted 7 July 2018

obtaining high photovoltaic response these GO based HTLs require high sintering temperature or vacuum based evaporation techniques (Acik and Darling, 2016). It has been occasionally revealed that, deposition of low temperature processed r-GO fails to cover the whole surface of the transparent conductive glass eventually providing opportunity for large defects at the interface with the perovskite absorber. These defects at the surface of r-GO eventually leads to potential recombination centres creating instability of the overall PSC. Moreover, the valence band of low temperature processed r-GO is −4.97 eV which has a huge energy mismatch with the perovskite compound valence band (−5.4 eV). This huge mismatch can hinder the potential collection of holes at the r-GO/perovskite interface and limit the photovoltaic performance of the overall PSC. To overcome these issues, we have recently reported with bilayer structured HTLs with r-GO and organic polymer, poly(triarylamine) (PTAA) and shown promising results (Zhou et al., 2017). However, in the long run, organic compounds as HTLs might not be a suitable choice due to their vulnerable behaviour in ambient environment. With an objective to obtain higher photovoltaic performance and potential commercialization aspect, insertion of an inorganic HTL with higher valence band than r-GO may increase the hole collection. CuSCN, a *p*-type material with a valence band of −5.30 eV and bandgap of 3.6 eV (Jung et al., 2015) can be considered as one of the potential interfacial material to transport hole faster in this aspect. However, to achieve maximum transparency, an ultrathin layer of CuSCN layer should be beneficial. The potential high bandgap with matched valence band level with the corresponding perovskite absorber can provide sufficient transparency across the UV–Vis/NIR wavelength region and lower loss caused by parasitic absorption.

Here in this work, we introduce an ultrathin CuSCN layer as an efficient interlayer in low temperature processed r-GO based inverted planar PSCs. We have systematically optimized the thickness of CuSCN interlayer at the r-GO/Perovskite interface to enhance the photovoltaic performance of the PSC with a surface area of 1.02 cm^2. With matched energy level, the r-GO/CuSCN bilayer HTM successfully prevented the recombination at the interface with the $MAPbI_3$ absorber layer. Simultaneously, the r-GO/CuSCN bilayer HTL leads to faster hole extraction as confirmed by the photoluminescence study. The r-GO/CuSCN bilayer HTL based PSC showed a high power conversion efficiency (PCE) of 14.28% with photovoltaic parameters of open circuit voltage (V_{OC}) = 1.031 V, short circuit current density (J_{SC}) = 18.21 mA cm^{-2}, fill factor (FF) = 0.761. The PCE of the r-GO/CuSCN bilayer HTL based PSCs were higher than that of the individual r-GO based PSCs (PCE = 9.52%). Additionally, enhanced stability has been observed for the r-GO/CuSCN bilayer HTL based PSCs retaining over the 90% initial efficiency after 100 h light soaking.

2. Experimental

2.1. Materials

The following chemicals were obtained from commercial suppliers and used as received: PbI_2 (99%, Sigma–Aldrich), MAI (> 98%, Tokyo Chemical Industry Co., Japan), PCBM (99.5%, Lumtec Co., Taiwan), bathocuproine (Wako), Graphene oxide (2 mg mL^{-1}, Sigma-Aldrich), Super dehydrated dimethylsulfoxide (DMSO), *gamma*-Butyrolactone (GBL), toluene, and methanol were purchased from Wako, Japan. All the chemicals were used as received without further purification.

2.2. Device fabrication

The r-GO film was prepared on top of the ITO glass from a 0.5 mg mL^{-1} aqueous solution and annealed at 150 °C for 90 min to form a 2.5 nm thick r-GO film. After cooling down the r-GO films to room temperature, a 10 nm uniform CuSCN layer (from a solution of 10 mg mL^{-1} in diethyl sulfide) was obtained by spin-coating at 6000 rpm for 60 s on top of it and was annealed for 30 min in air. The thickness of the CuSCN layer between 10 nm and 40 nm was obtained by controlling the rotation speed of the spin coater between 3000 and 6000 rpm (see Table S2). Then the r-GO/CuSCN coated ITO glasses were cooled down to room temperature and transferred to a N_2 glovebox. A $MAPbI_3$ precursor solution (100 µL) consisting of PbI_2 (922 mg) and CH_3NH_3I (318 mg) dissolved in 2 mL of 3:7 (v/v) DMSO/GBL was spread over the r-GO/CuSCN film and spin-coated with two steps of spin-coating, first at 1000 rpm for 12 s and then 5000 rpm for 30 s. 100 µL of toluene was dropped onto the perovskite-coated r-GO/CuSCN film 10 s prior to the start of second stage of spin-coating at 5000 rpm. Finally, the film was annealed at 100 °C for 30 min resulting in a 400 nm thick $MAPbI_3$ layer. All the $MAPbI_3$ layers has been fabricated with similar thickness regardless in the thickness variation of HTL layers. After cooling down to room temperature, a solution of PCBM in chlorobenzene (20 mg mL^{-1}) was spin-coated on top of the film at a rotation speed of 1000 rpm for 30 s. A saturated methanol solution of bathocuproine (140 µL) was spin-coated onto the PCBM coated film with spin rotation of 6000 rpm for 30 s. The PSC fabrication was completed by thermal evaporation of a 100 nm thick film of Ag as the cathode.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.solener.2018.07.022.

2.3. Characterization

The thickness of the fabricated r-GO, CuSCN and r-GO/CuSCN films were measured with J.A. Woollam (M-2000X) elipsometer. The angel of incident light was set at 45° for reflectance measurement of thickness of all the films. FESEM images were obtained with a Hitachi S-4800 field emission scanning electron microscope. The atomic force microscopy images were obtained with JSPM-5200 scanning probe microscope.

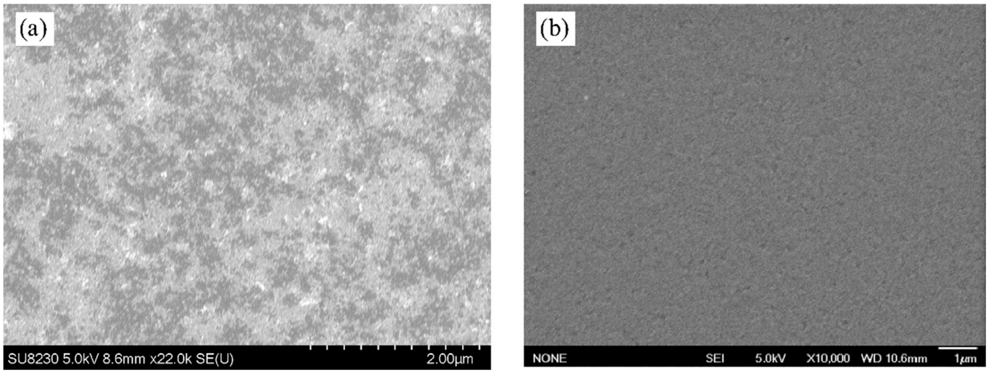

Fig. 1. SEM surface images of (a) ITO/r-GO and (b) ITO/r-GO/CuSCN.