Journal of Industrial and Engineering Chemistry 52 (2017) 243–250

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Fogging, reflection, and dust-free transparent conducting glasses based on superhydrophilic nanotextures for organic photovoltaics

Eun Chong Kim[a], Seok-In Na[a,**], Jung Tae Park[b,*]

[a] Professional Graduate School of Flexible and Printable Electronics, Polymer Materials Fusion Research Center, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 54896, South Korea
[b] Department of Chemical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, South Korea

ARTICLE INFO

Article history:
Received 30 October 2016
Received in revised form 20 March 2017
Accepted 25 March 2017
Available online 4 April 2017

Keywords:
Organic photovoltaic (OPV)
Superhydrophilic
Silica
Fogging-free
Self-cleaning

ABSTRACT

We present the preparation of high-efficiency organic photovoltaics (OPVs) using functional transparent conducting oxide glasses (functional TCOs) based on superhydrophilic nanotextures under fogging conditions. The superhydrophilic nanotextures are easily prepared with spin-coating of aged colloidal silica suspensions on the non-conducting side of indium tin oxide glasses (ITOs). PEDOT:PSS is used as a hole transport layer (HTL) in OPVs with PTB7/$PC_{71}BM$ as a bulk hetero-junction layer (BHJ layer). The OPVs based on functional TCOs were confirmed by atomic force microscopy (AFM), scanning electron microscopy (SEM), water contact angle, UV–vis spectroscopy, and external quantum efficiency (EQE) measurements. Compared with the conventional TCOs, the functional TCOs, which have superhydrophilicity, axial gradient in refractive index, substantially suppress fogging and reduce reflection, leading to significantly improved light harvesting. The efficiency of OPVs based on functional TCOs (4.4%) were higher than those of OPVs with conventional TCOs (2.9%) under fogging conditions. This work has also demonstrated on superhydrophilic nanotextures based functional TCOs with excellent dust-free and self-cleaning performance.

Introduction

Organic photovoltaics (OPVs) based on bulk heterojunction of polymer and fullerene are promising solar energy source due to their low cost, light weight, mechanical flexibility, solution processability, and large-area manufacturing compatibility [1–3]. State-of-the-art OPVs have shown a high energy conversion efficiency of 11% under 100 mW/cm^2 [4]. The conventional structure of OPVs is typically composed of indium tin oxide (ITO) substrate, hole transport layer (HTL), bulk hetero-junction layer (BHJ layer), and a metal cathode. Research on OPVs has been focused on achieving a higher light to electricity conversion efficiency based on the design of suitably modified substrate [5–7], the fabrication of novel HTL [8–10], the synthesis of functional BHJ layer [11–14], and the preparation of enhanced electronic metal cathode [15–17]. However, further enhancements of OPV efficiency and stability are still remained as an active area of scientific research.

Glass based substrates are fundamental materials with thousands of practical applications such as automobiles, vehicles, buildings windows, optical, display, and photovoltaic devices. Recently, several studies have focused on the preparation of superhydrophobic structure on substrate to improve its fogging, reflection, dust-free properties. For example, fly-eye bio-inspired inorganic nanostructures were synthesized *via* a two-step self-assembly approach, which has low contact angle hysteresis and improved fogging-free properties [18]. Recent investigations into the fish-scale bio-inspired multifunctional ZnO nanostructures have demonstrated a significant surface wettability with self-cleaning properties [19]. Also, the ultrathin low-molecular-weight polydimethylsiloxane layer exhibited an excellent fogging-free performance on spectacle lenses without any effects on the optical prescription [20]. Particularly, fogging, reflection, dust-free managements of substrates are an indispensable component to reduce or suppress reflection losses, to enhance the amount of incident photons into the devices, and hence to improve the light harvesting efficiency of solar cells. For example, the 3D nanocone reflection-free films on the CdS/CdTe solar cells exhibited self-cleaning function and high efficiency [21]. Also, it was reported that

---

[*] Corresponding author. Fax: +82 2 450 8895.
[**] Corresponding author. Fax: +82 63 270 2341.
E-mail addresses: nsi12@jbnu.ac.kr (S.-I. Na), jtpark25@konkuk.ac.kr (J.T. Park).

http://dx.doi.org/10.1016/j.jiec.2017.03.053

bifunctional moth-eye nanopatterned structure on the ssDSSCs could significantly boost the light harvesting and result in enhanced cell efficiency of more than 7% [22]. Recently, the inverted micro-pyramidal structured polydimethylsiloxane anti-reflection layers were prepared for enhancing the perovskite solar cell efficiency [23]. However, most of these preparation processes involve sophisticated multi-steps and are often time consuming, which poses a hindrance for practical applications. Therefore, a great challenge for researchers is to develop a more conventional coating approach for future photovoltaic applications such as building integrated photovoltaics (BIPV). An alternative approach to induce fogging, reflection, dust-free properties is the preparation of superhydrophilic nanostrucrures on the devices. It is known that the nanoporosity as well as an abundance of hydroxyl groups on the high specific surface area of the superhydrophilic nanostrucrures can lead to enhance the fogging and dust-free properties [24]. Also, single layer reflection-free coatings inspired by the idea of a continuously graded-refractive index profile are one of the most researched areas of an optical device since this approach is simple and cost effective and therefore more suitable for practical optical applications [25]. For example, all nanoparticle films were prepared *via* layer-by-layer deposition of TiO_2 and SiO_2 nanoparticles for enhanced fogging and reflection-free properties with self-cleaning [26]. The polyvinylpyrrolidone and aminopropyl-functionalized, nanoscale clay platelets based films were superhydrophilic and showed more than 90% transmission of visible light, as well as excellent fogging-free properties [27]. Also, it was reported that controlled aggregation of pH-neutralized silica nanoparticle solutions followed by spin coating provides a straightforward method to prepare single layer reflection-free coatings [24].

In this report, we investigated the superhydrophilic nanotexture based functional transparent conducting oxide glasses (functional TCOs) and studied their effects on the OPVs under fogging conditions. The superhydrophilic nanotextures were fabricated by spin-coating of aged colloidal silica suspensions on the non-conducting side of ITOs. The OPVs based on functional TCOs were characterized in detail using AFM, SEM, water contact angle, UV–vis spectroscopy, and EQE analysis. The photovoltaic performance of OPVs fabricated with functional TCOs is also reported here. To the best of our knowledge, the functional TCOs based on superhydrophilic nanotextures incorporated in OPVs, which can multiply the fogging, reflection, and dust-free properties, have not been reported.

Experimental section

Material

LUDOX TM-40 (40 wt% silica suspension in H_2O, 22 nm) and hydrochloric acid (HCl) were purchased from Sigma-Aldrich (St Louis, MO). Indium tin oxide glass (ITO) was purchased from AMG Co. Ltd. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios PVP AI 4083) was purchased from Heraeus. Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno[3,4-b]thiophenediyl}) (PTB7, ~97 000 M_w) was purchased from 1-Material. [6,6]-Phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) was purchased from Nano-C. 1,8-Diiodictance was purchased from Tokyo Chemical Industry Co. Ltd. 2-Propanol, acetone, and chlorobenzene were purchased from J. T. Baker. Deionized water (>18 MΩ m) was obtained with a water purification system made by Millipore Corporation. All chemical and solvents were reagent grade and used as received. Unless noted otherwise, all experiments were carried out under ambient conditions in air.

Preparation of functional TCOs

Functional TCOs were fabricated by slightly modifying a previously reported procedure [28]. For solutions that were aged, LUDOX TM-40 (40 wt% silica suspension in H_2O, 22 nm) was adjusted to pH 7.0 by using HCl, and the solution was aged for 2 h at 50 °C. This procedure was required to reduce the negative surface charge on the silica nanoparticles and impart nanoparticle aggregation through the condensation process of silanol groups on the nanoparticle surface. This aged solution was subsequently diluted to 5 wt% for spin coating. Separately, the ITOs were cleaned with acetone, deionized water, and 2-Propanol. And then, as-prepared aged colloidal silica suspensions was spin-coated onto the non-conducting side of the ITOs at 2000 rpm and was dried at 70 °C for 30 min.

Fabrication of OPVs

OPVs were fabricated according to our previous studies [29,30]. First, the functional TCOs were treated with UV/O_3 plasma for 20 min. PEDOT:PSS as the hole transport layers (HTLs) on the conducting side of the functional TCOs was prepared by spin coating at 5000 rpm for 40 s under atmospheric conditions and subsequently annealed at 120 °C for 10 min. A solution composed of 10 mg of PTB7, 15 mg of $PC_{71}BM$, and 1,8-diiodictance (5 vol%.) in 1 mL of chlorobenzene was also prepared, and the resulting blend solution was spin-coated on the HTLs at 2000 rpm for 60 s for the fabrication of a bulk hetero-junction layer (~100 nm). This was followed by solvent evaporation for 120 min and thermal annealing at 110 °C for 10 min in N_2. Finally, the thermal evaporation of a metal cathode having Ca (20 nm)/Al (100 nm) was performed under vacuum at 10^{-6} Torr. In addition, conventional TCO based OPVs were used as control group.

Characterization

Surface morphologies of superhydrophilic nanotextures were conducted by atomic force microscope (AFM) using a XE7 (Park system) operated in tapping mode with a silicon cantilever. Scanning electron microscope (SEM) (S-4800, Hitachi) was used to examine the topology of superhydrophilic nanotexture coated functional TCOs. The refractive index of superhydrophilic nanotextures was determined using a spectroscopic ellipsometer, Alpha-SE and the Complete EASE software package (J. A. Woollam). The wettability of superhydrophilic nanotextures was characterized by the measurement of water contact angles on their surfaces (Phoenix 150, surface electro optics). Distilled water droplets of 10 mL were dropped carefully onto the film surfaces. UV–vis spectroscopy was measured with spectrophotometer (Mega 900, Scnico) in the range of 300–800 nm. Cell performance was measured using a Keithley 2400 instrument operated using a xenon light source and AM 1.5 global filter. A reference Si solar cell certified by the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc.) was used for calibration for accurate measurement. And, the external quantum efficiency (EQE) was measured as a function of wavelength using a specially designed EQE system (IQE-200, Oriel).

Results and discussion

Preparation of functional TCOs

In our architecture, 1. functional TCO, 2. PEDOT:PSS, 3. PTB7/$PC_{71}BM$, 4. Ca/Al were stacked from the bottom to the top electrodes, as shown in Scheme 1. The functional TCO was prepared through the deposition of aged colloidal silica suspensions based superhydrophilic nanotextures on the non-conducting