

# Efficient light harvesting in inverted polymer solar cells using polymeric 2D-microstructures

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## ABSTRACT

In this paper, we report effectiveness of microstructured scattering layer and their efficient light trapping mechanism for performance improvement of polymer solar cells (PSCs). Our simple roll-to-roll processed polymeric scattering layer is an intrinsic and economical way to harvest more light in the photoactive layer of PSC's. An inverted polymer solar cell with microstructured scattering layer and photoactive layer of poly[4,8-bis(5-2-ethylhexyl)thiophen-2-yl]benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thioph-ene-(2-carboxylate-2-6-diyl)(PTB7-Th) and [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PC<sub>60</sub>BM) exhibit a maximum power conversion efficiency of 8.60% under simulated AM 1.5G illumination at light intensity of 100 mw/cm<sup>2</sup>. A significant improvement of over 15% in short circuit current density of the solar cell devices is achieved by means of suppressing Fresnel reflection at the glass and air interface. In addition, wetting properties and optical simulation of the PSC's with and without scattering layer are performed using water contact angle measurement and SETFOS 4.1 module. We expect that this methodology will be advantageous for the development of future organic solar cells.

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## 1. Introduction

Recently, advanced polymer bulk heterojunction (BHJ) solar cells generated huge interest due to its enormous potential to become a future cost effective energy source. Because of numerous advantages like light weight, low cost fabrication and excellent lifetime, a wide variety of research work is reported on the synthesis of new donor, interfacial materials with proper device engineering; to improve the power conversion efficiency (PCE) towards commercialization limit [1–11]. The PCE of single junction solar cells touched more than 10% [9–11]. However, further PCE enhancement is still desirable for the commercialization of such fascinating and encouraging technology.

Because of thickness limitation of photoactive layer and low diffusion length maximum solar light harvesting is not possible regardless of high absorption coefficient of electron donor material. Several approaches for efficient light harvesting and improvement in overall performances of polymer solar cells (PSCs) are proposed using appropriate interfacial engineering. These studies include numerous air stable and highly translucent interfacial layers along with doped charge selective layers for tuning the energy levels. It competently reduces the recombination of holes and electrons with enhancement in the charge carrier extraction processes [12–17]. Additional optical loss at the layer interfaces is the main hurdle in improving light

absorption probability of polymer photoactive layer. Indeed, most of the incoming light is cramped and reflected from external glass substrate because of the index mismatch between air and glass substrate. Therefore, the addition of light in-coupling technique is a progressively prominent approach. It improves light trapping and complete performances of the solar cells. Very few literatures are reported on in-coupling layers and antireflective coatings for the improvement in absorption efficiency. Particularly, the moth-eye nanostructures, photonic crystals, surface plasmons approaches are used to suppress Fresnel reflections at the external interface and to trap more light in the photoactive layer [18–22]. This strategy is applicable over a broad spectral range and wider angle of incidence. Different geometry of nanostructures similar to biomimetic moth-eye, V-shaped and random textured surface have been fabricated from polymer, ZnO, metal (Au, Ag) and used as an anti-reflective surface in optoelectronic applications [18,19,23–27]. Similarly, array of fused silica fiber and textured retro-reflective foil, microlens array are already reported for efficient light trapping in polymer solar cells [28–30].

A facile processed polymer nano/micro-structures at the external glass surface is an easy and effectual optical approach to enhance light trapping inside the photoactive layer. It is possible because of decreasing incident light reflection. However, reported light in-coupling schemes especially external nanostructured film showed limited improvement in PSC's performances. Recently, Tang et al. used an UV resin and ZnO based moth-eye nanostructures on the external glass surface and photoactive layer of PSCs to improve its overall performances without compromising the dark characteristics. The

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improvement in PCE and short circuit current density ( $J_{sc}$ ) for antireflective nanostructured film is reported as  $\sim 3.89\%$  to  $4.3\%$  only [18,19,23]. Similarly, Yu et al. reported 2D periodic inverted moth-eye nanostructured PDMS film for light in-coupling in PSCs. It demonstrates a significant improvement in PCE, especially by enhancing light absorption in the active layer [25]. However, most of the reported light in-coupling schemes have limitations in terms of performance improvement and processing. Thus, to guide more light into the photoactive layer and to achieve maximum light harvesting; simple, large area process and cost effective light in-coupling scheme needs to be developed.

Herein, we propose the fabrication of polymeric 2D-microstructured scattering layer (MSL) using facile roll-to-roll process and mold transfer method. The hemispherical microstructures with higher dimension than the incident light wavelength can easily refract light into the photoactive layer. It also helps to reduce light reflection at the glass surface. Because of the larger dimension of hemisphere (compared to the wavelength of incident light), light trapping mechanism can be examined using geometrical optics [22]. The fabricated MSL layer on glass surface exhibits an excellent optical property. Incorporation of MSL on the external glass surface of PSCs shows an improved light harvesting with more than 14% enhancement in PCE. Extensive simulation is done to study the scattering properties of microstructured layer. Photoactive layer thickness dependent optical simulation of PSCs with and without scattering layer agrees with experimental results.

## 2. Experimental section

### 2.1. Fabrication of 2D-MSL film

Fig. 1 shows the schematic representation of fabricated microstructured film using a mold transfer method. PDMS negative mold with uniform hemispherical structures was made according to the previously reported method [31]. Afterward, acrylic layer was formed using roll-to-roll process and then PDMS mold was applied on top of the acrylic layer with uniform pressure. After complete curing treatment, PDMS mold was detached. The SEM image of the fabricated microstructured film is shown in Fig. 2.

### 2.2. Device fabrication

To fabricate inverted PSC structure, patterned ITO coated glass substrates with sheet resistance of  $15 \Omega/\square$  were sequentially cleaned with acetone, isopropyl alcohol (IPA), and deionized water and subsequently, treated in ultraviolet ozone (UVO) for 10 min. Primarily, a ZnO solution was spin coated on top of the pre-cleaned ITO substrates at 3000 rpm followed by annealing at  $150^\circ\text{C}$  for 30 min in ambient atmosphere. Then the substrates were transferred to the nitrogen filled glove box for photoactive layer deposition. Successively, PTB7-Th (1-material):PC<sub>60</sub>BM (Sigma Aldrich) (110 nm) was spin-coated at 1600 rpm on top of the ZnO layer. A blend solution of PTB7-Th and PC<sub>60</sub>BM was prepared in mixed solvents 1,2-dichlorobenzene (99%, DCB) and 1,8-diiodooctane (DIO) (97:3,  $v(\text{volume}):v(\text{volume})$ ) and

the total concentration was 25 mg/ml. Afterward, photoactive layer coated substrates were transferred into high vacuum pressure ( $3.0 \times 10^{-7}$  Torr) thermal evaporation chamber for the deposition of molybdenum trioxide (MoO<sub>3</sub>) and Aluminum (Al). The deposition rate of MoO<sub>3</sub> and Al was maintained at  $0.3 \text{ \AA s}^{-1}$  and  $2.5 \text{ \AA s}^{-1}$ . Subsequently, all devices were encapsulated by a transparent glass cover by using an UV curable epoxy as the sealing material inside the nitrogen filled glove box. Finally, separately made polymeric microstructured film was incorporated on top of the external light incident surface of PSC using index-matching fluid.

### 2.3. Device characterization

All device measurements were carried out at room temperature and ambient atmosphere. The photo-performance of fabricated devices was measured using a solar simulator with an Air Mass 1.5 G irradiation intensity of  $100 \text{ mW/cm}^2$ . The active area of the device was  $0.2 \times 0.2 \text{ cm}^2$ . A xenon light source was used to give a simulated irradiance of  $100 \text{ mW cm}^{-2}$  (equivalent to an AM1.5G irradiation). The External Quantum Efficiency (EQE) measurements were performed using the EQE system (Model 74000) obtained from Newport Oriel Instruments USA and a HAMA-MATSU calibrated silicon cell photodiode was used as a reference diode. The wavelength was controlled with a monochromator in the range 300–1600 nm. All the thickness measurements were carried out using a surface profiler (Alpha step). The surface morphology of the MSL was analysed using scanning electron microscopy (SEM) (Hitachi, S-4700). The total reflectance spectra were measured using UV/vis/near-IR spectrometer (Perkin Elmer Lambda 650) equipped with an integrating sphere. The reflectance measurements were performed at room temperature for 300–800 nm wavelength range. For total reflectance measurements, light was irradiated on the glass (Glass/ITO) and MSL (MSL/Glass/ITO) side of both samples at  $8^\circ$  incidence angle.

### 2.4. Theoretical evaluation

The optical properties of PSCs were calculated using commercially available semiconducting emissive thin film optics simulator (SETFOS 4.1) module. It is used for the design and development of optoelectronic thin-film devices (OLED and OSC). For the theoretical evaluation of absorption and reflection properties, fabricated solar cell structure (see Fig. 3) was also designed with optimized thickness of transport layers using SETFOS 4.1 simulation module. The Lambertian scattering model and AM1.5 Sun spectrum was employed to study the surface scattering properties of glass/air interface. The  $n$  and  $k$  values of the photoactive layer (PTB7-Th:PC<sub>60</sub>BM) was measured using the spectroscopic ellipsometer while,  $n$ ,  $k$  values of other materials were applied from the SETFOS material library.

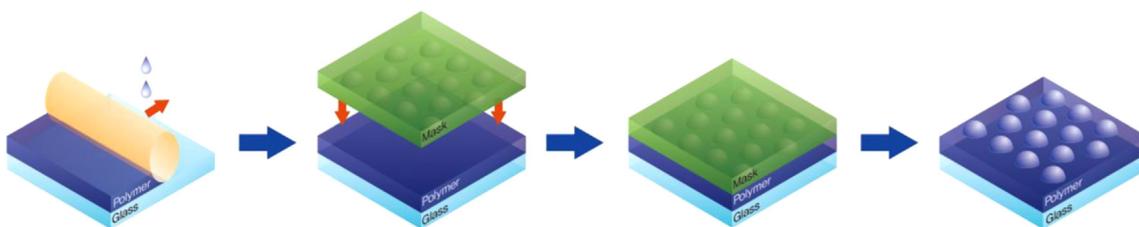


Fig. 1. Schematic depiction of the fabrication of hemispherical microstructured layer using roll to roll and mold transfer process.

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