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ORIGINAL REPORT



## Low-cost light manipulation coatings for polymer solar cell photocurrent increase under various incident angles

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### ABSTRACT

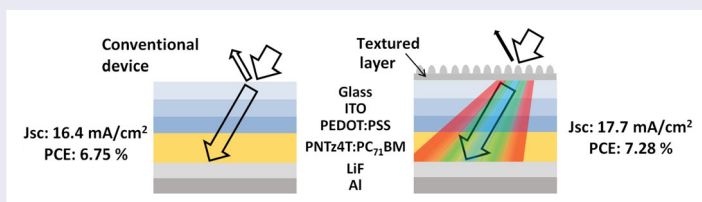
We fabricate self-assembled templates to produce textured polydimethylsiloxane (PDMS) with quasi-random dimension distributions which are employed as light manipulation coatings in polymer solar cells (PSCs). When deposited at the PSC glass/air interface, PDMS films with microdome-like structures enhance the short-circuit current density ( $J_{sc}$ ) by 7.9% through combined anti-reflective and scattering effects. The PSC power conversion efficiency can thus be improved from 6.75% to 7.28% and a maximum  $J_{sc}$  increase of 21% is observed for incident light tilted by 30 degrees. We compare structures with different diameter dispersities and confirm that quasi-randomness in textured coatings can increase their light scattering ability.

### ARTICLE HISTORY

Received 1 August 2018

### KEYWORDS

Nanofabrication; polymer solar cells; self-assembly; light manipulation



### IMPACT STATEMENT

Unlike costly lithographic techniques, this self-assembled approach opens the path to low-cost fabrication of quasi-random microtextured coatings for PSCs to efficiently harvest sunlight throughout the day (at various incident angles).

## Introduction

Owing to the small amounts of active materials employed during device fabrication and their potential for roll-to-roll production, polymer solar cells (PSCs) are often considered to be low-cost alternatives to silicon photovoltaic technologies [1,2]. Recent advances in polymer chemistry resulted in large enhancements of their power conversion efficiencies (PCEs) that now overcome the milestone value of 10% [3–5]. For instance, PSCs employing a naphthobisthiadiazole-alt-quaterthiophene copolymer (PNTz4T) and a fullerene derivative absorbing visible light (PC<sub>71</sub>BM) produce PCEs up to 10.1% when 300 nm-thick active layers are used [3]. As advanced chemistry is necessary to produce these active materials, their cost is gradually increasing along with the device PCEs. Improving the performances of thin active

layer ( $\sim 100$ – $150$  nm) PSCs can be an efficient method to maintain a relatively low production cost. Thin PNTz4T:PC<sub>71</sub>BM uniformly absorb visible light and maintain a relatively high transparency, thus having great potential for the fabrication of semi-transparent photovoltaic windows [6,7].

Previous studies have demonstrated that regularly arranged nano- and micro-textured optical coatings can be employed at the PSC glass/air interface to improve their device performances [8–11]. Although efficient light manipulation in PSCs could be achieved using cost-effective processes such as monodisperse particle assemblies [9,12] or nanoimprint lithography [13], phase separation in polymer blend thin films, which can produce various textured surfaces at a very low fabrication cost [14,15], have not yet been tested as light manipulat-

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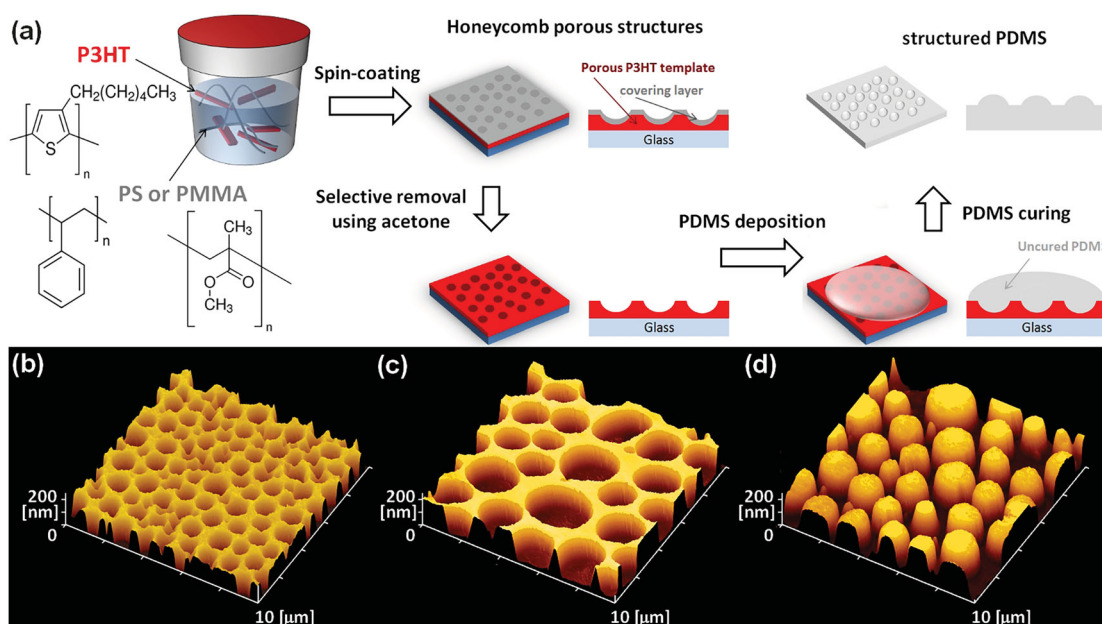


**Figure 1.** (a) Schematic representation of nanoPDMS and microPDMS fabrication using self-assembled porous templates prepared by mixing P3HT with PS or PMMA, respectively; AFM images of (b) nanopororous, (c) microporous templates and (d) microPDMS.

ing coatings in PSCs. We have previously demonstrated that porous poly(3-hexylthiophene) (P3HT) films with pore diameters ranging from 150 nm to 2  $\mu\text{m}$  can be produced using phase separated polymer blends composed of P3HT with polystyrene (PS) or poly(methyl methacrylate) (PMMA) [16,17]. The pore diameter in these thin films can be engineered using polymer molecular weight or relative concentration of the various polymers. Furthermore, miscibility of the two polymers in the blends controls the quasi-randomness of pore diameter dispersity and higher dispersities are obtained for the less miscible P3HT:PMMA blends. Despite the fact that quasi-random textured surfaces are suspected to produce more efficient light manipulation than ideal structures [18], and that previous studies suggest that phase separated polymer thin films have a great potential for the fabrication of anti-reflective layers [14,15], so far there is no evidence that they can be successfully employed to enhance the performances of PSCs.

Here, we present a simple low-cost approach based on phase separated polymer blends for the fabrication of hexagonally arranged porous films with quasi-random pore diameters (Figure 1). These low-cost templates are used to produce polydimethylsiloxane (PDMS) films with nanoscale domes (nanoPDMS) or a mixture of nano- and microscale domes (microPDMS) which all have similar dome heights around 250 nm. When nanoPDMS and microPDMS are placed at the glass/air interface of thin PNTz4T:PC<sub>71</sub>BM, they produce an average  $J_{sc}$  enhancement of 6.2% and 7.9%, respectively which can be attributed to a combination

of anti-reflective effect and light scattering. To understand whether quasi-randomness yields stronger light scattering, we compare simulated active layer absorbance increase when using ideal textured optical coatings with experimental results from nanoPDMS and microPDMS. The larger dome diameter dispersity of microPDMS produces enhanced light scattering effects which induce a PCE increase from 6.75% for the bare devices to 7.28% under normal irradiance conditions. Unlike bare PSCs, which exhibit a significant decrease in performances when tilting the incident light, microPDMS-covered PSCs maintain high efficiencies when light is inclined up to 30 degrees.

## Materials and methods

### Fabrication of porous templates and PDMS replica

Porous templates were fabricated by blending P3HT (Merck, Mw  $\sim$  197,500) with PS (Sigma-Aldrich, Mw  $\sim$  35,000) or PMMA (Sigma-Aldrich, Mw  $\sim$  15,000). Templates for nanoPDMS and microPDMS were produced employing 1:1 weight ratios of P3HT:PS and P3HT:PMMA blends, respectively. The total polymer concentration was 30 mg/ml in chlorobenzene solutions that were spin-coated at 1000 rpm for 60s on  $2.5 \times 2.5 \text{ cm}^2$  glass substrates. The substrates were then soaked in acetone for 5 min, followed by surface cleaning with 0.5 ml of acetone to remove the PS or PMMA phases. Except from a small area at the edges of the substrates, the template porous films exhibit good uniformity for

average pore diameters and density, which indicates that the process could be scaled-up to larger spin-coated areas.

The templates were placed in a container that was filled with a 10:1 weight ratio of PDMS base and curing agent (Sylgard® 184, Dow Corning). The containers were heated at 80°C for 2 h to induce the formation of the structured PDMS. Film thickness was controlled to 3 mm by the amount of mixture deposited in the container. For flat PDMS, a similar procedure was performed on cleaned glass substrates. The free-standing PDMS layers are gently peeled off from the substrates and the porous templates can be reused up to 50 times without any observed damage to their surface.

### PSC fabrication

Patterned ITO-covered glass substrates (Atsugi Micro) were cleaned using a standard procedure (ultrasonication in acetone, detergent, deionized water, isopropanol and hot isopropanol) and exposed to a surface plasma treatment before a 40 nm-thick PEDOT:PSS layer (Heraeus, Clevios AI4083) was spin-coated on their surfaces at 4000 rpm for 30 s. PNTz4 T was synthesized according to previously published procedures [3]. PC<sub>71</sub>BM was purchased from Luminescence Technology Corp. To produce 150 nm-thick active layers, PNTz4 T and PC<sub>71</sub>BM were blended in a 1:2 ratio (total concentration: 9 mg/ml in 1,2-dichlorobenzene) and spin-coated at 400 rpm for 30 s followed by 2000 rpm for 3 s. After complete drying of the active layers in high vacuum ( $< 10^{-3}$  Pa) overnight, 0.5 nm of LiF and 70 nm of Al were sequentially evaporated as top cathode and the devices were encapsulated inside a nitrogen-filled glovebox. The device area, defined by the overlap between the ITO pattern and the metal electrode, corresponds to 0.02 cm<sup>2</sup>.

### Characterizations and simulations

Experimental details for photovoltaic characterization, AFM measurements, direct, total and angle-dependent light transmissions (Figure S1), as well as active layer absorbance simulations with ideal textured PDMS (Figures S2 and S3) can be found in the Supplementary Material file.

## Results and discussion

Previous studies have demonstrated that when dome-like arrays are deposited at an interface, continuous refractive index gradients can be successfully generated [19]. To reduce optical losses at the glass/air interface, the material employed as optical coating should have a refractive index between those of glass (1.54) and air (1.00). PDMS has a refractive index of 1.4 and cm-thick PDMS films only absorb wavelengths below 350 nm [20]. Consequently, even when thick PDMS films are employed, absorption from PDMS should not affect the amount of sunlight (AM1.5) transmitted through the optical coatings. Anti-reflective films are commonly conceived with sub-wavelength dome dimensions but several studies have demonstrated the possibility to employ domes with much larger diameters to increase the performances of PSCs [12]. We first investigate the anti-reflective properties of flat PDMS, nanoPDMS and microPDMS by measuring the total light transmission enhancement when these coatings are placed on a glass substrate. By using an integrating sphere (Figure S1), we measure light transmitted through the glass when coated with the various PDMS films (T) and compare these to the light transmitted through bare glass (T<sub>0</sub>). The results presented in Table 1 clearly indicate that textured PDMS coatings produce higher anti-reflective properties than flat PDMS with transmitted light enhancements of 2.5% and 2.2% for nanoPDMS and microPDMS, respectively. NanoPDMS coatings with smaller average dome diameters of 500 nm and a more adequate refractive index profile transmit light slightly more efficiently than textured microPDMS with larger average dome diameters of 1700 nm.

To verify the potential of nanoPDMS and microPDMS as light manipulating layers for PSCs, we measured the photovoltaic parameters of thin PNTz4T:PC<sub>71</sub>BM active layer PSCs, in which the various free standing PDMS optical layers were fixed at the glass substrate/air interface. To remove errors related to device reproducibility, the same devices, which have reached a stable performance regime, were used to characterize all optical coatings. We further verified that the devices have not degraded during the measurement by collecting the photovoltaic parameters of the bare devices before fixing and after removing the optical coatings on their back-sides. A very small performance variation (below 0.05%)

**Table 1.** Relative increase in light transmission through glass upon deposition of the optical coatings at the glass/air interface and photovoltaic parameters of bare and coated PNTz4T:PC<sub>71</sub>BM PSCs. Jsc<sub>0</sub> corresponds to the Jsc of bare PNTz4T:PC<sub>71</sub>BM PSCs.

| Coating   | T/T <sub>0</sub> (%) | Jsc (mA/cm <sup>2</sup> ) | Jsc/Jsc <sub>0</sub> (%) | Voc (mV) | FF (%) | PCE (%) |
|-----------|----------------------|---------------------------|--------------------------|----------|--------|---------|
| no PDMS   | 100                  | 16.41                     | 100.0                    | 715      | 57.5   | 6.75    |
| flat PDMS | 101.1                | 16.72                     | 101.8                    | 716      | 56.9   | 6.81    |
| nanoPDMS  | 102.5                | 17.42                     | 106.2                    | 718      | 57.4   | 7.18    |
| microPDMS | 102.2                | 17.71                     | 107.9                    | 718      | 57.2   | 7.28    |

was measured, confirming that the collected data for the optical coatings can be accurately attributed to light absorption enhancements.

The J-V curves in Figure 2(a) and photovoltaic parameters in Table 1 indicate that the open-circuit voltage ( $V_{oc}$ ) and fill factor (FF) of the PNTz4T:PC<sub>71</sub>BM PSCs are not affected by fixing additional PDMS layers at their glass/air interface. Consequently, for the remaining part of this study, we will focus on  $J_{sc}$  increases. When using the PDMS optical coatings at the glass/air interface of the PSCs, the observed  $J_{sc}$  enhancements are larger than the increases in total transmitted light ( $T/T_0$ ) measured previously (Table 1). In particular, to understand the large  $J_{sc}$  increases of 6.2% and 7.9% measured for nanoPDMS and microPDMS, the light scattering abilities of these optical coatings should be taken into account. To estimate the contribution from light scattering on the  $J_{sc}$  increase, we performed computational simulations of the active layer absorbance of PNTz4T:PC<sub>71</sub>BM PSCs with and without PDMS optical coatings (Figure 2(b)). The dome array employed for the simulation has a dome height, dome radius and dome packing radius of 240, 250 and 450 nm, respectively (schematic representation in Figure S2). These dimensions correspond to the average values of the dome structure present on the nanoPDMS surface. The computed results predict a 2.7% increase in absorbance caused by light scattering when employing a nanoPDMS-like ideal dome structure. The combination of anti-reflective properties (2.5%) and computed scattering properties (2.7%) still cannot account for the larger  $J_{sc}$  increase (6.2%) measured through the J-V characteristics of the devices.

Previous studies suggest that quasi-random textures may produce stronger scattering than highly ordered ones [18]. As the computational method is based on pre-

defined ideal structures, it cannot account for the quasi-randomness which is relatively large for both nanoPDMS and microPDMS having dome diameter dispersities of 0.43 and 0.53, respectively. Here, we define dome diameter dispersity as the ratio of the diameter standard deviation over the mean value of diameter. Dispersity is equal to 0 for the ideal structures employed in the simulation. We hypothesize that the mismatch between  $J_{sc}$  enhancements and computed scattering abilities could be related to the quasi-randomness of nanoPDMS and microPDMS structures.

In fact, the direct transmission spectra through glass confirm that a decrease in reflection at the glass/air interface can be observed for wavelengths above 600 nm when employing nanoPDMS and microPDMS coatings (Figure 3(b)). However, for sub-600 nm wavelengths, both nanoPDMS and microPDMS display decreases in direct transmittance.

As PDMS is transparent in the wavelength range we study here (380–780 nm), which is relevant to PNTz4T:PC<sub>71</sub>BM active layer absorption and sunlight irradiance (AM1.5), we can exclude the hypothesis that these decreases are related to variations in PDMS thickness. Under normal incident light conditions, strong light scattering can be observed for microPDMS-coated glass and the transmitted light collected at 15, 20, 25 and 30 degrees displays quasi-monochromatic peaks which red-shift with increasing detection angle (Figure 3(c)). Although a similar behavior can be found in nanoPDMS-coated glass, the amount of scattered light is much lower compared to microPDMS-coated glass. To quantify scattering by these optical coatings, we define the transmitted light scattering capacity ( $C_s$ ) as the ratio between the total transmitted light ( $T$ ) and the direct transmitted light ( $T_{direct}$ ). We obtain  $C_s$  values of 0.7% and 7.2% for

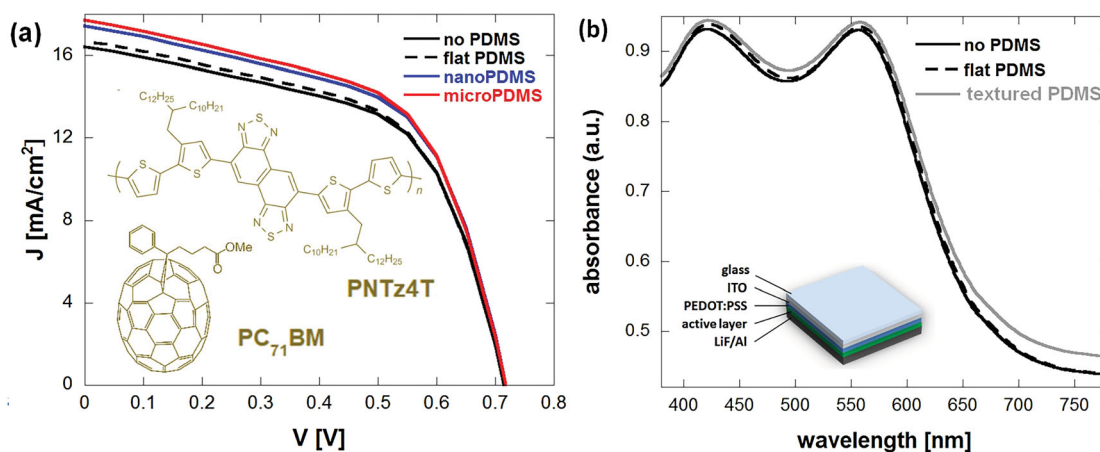


**Figure 2.** (a) Experimental J-V curves for bare and PDMS-coated PNTz4T:PC<sub>71</sub>BM regular architecture PSCs and (b) Simulated absorbance spectra of the bare and coated active layers. The inset of Figure 2(b) corresponds to the regular device architecture employed in this study.

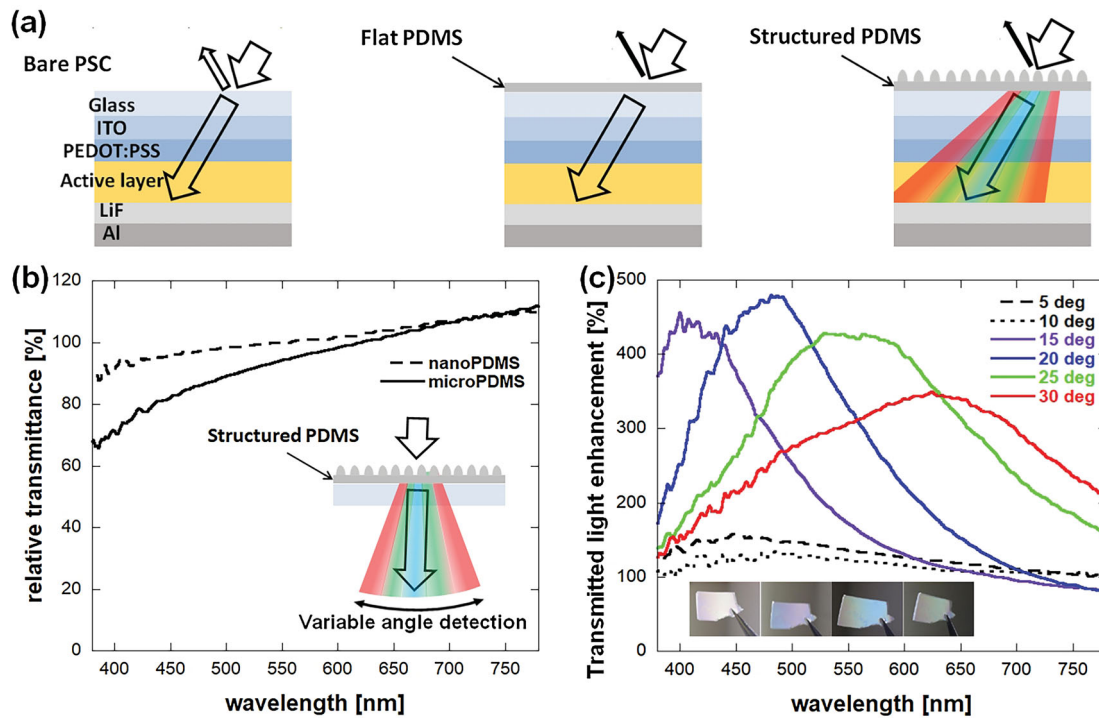


**Figure 3.** (a) Schematic representations of transmitted light for bare and PDMS-covered PSCs; (b) Relative transmittance of nanoPDMS and microPDMS for incident light and detection along the normal direction; and (c) Transmittance through microPDMS measured at various transmitted angles with incident light normal to the substrate. The insets of Figures 3(b,c) are a schematic representation of the measurement conditions and photographs of microPDMS taken at various angles, respectively.

nanoPDMS and microPDMS, respectively, confirming that quasi-random structures with higher dome diameter dispersities yield stronger transmitted light scattering. The larger  $J_{sc}$  enhancement when PSCs are coated with microPDMS (7.9%) as compared to nanoPDMS (6.2%) also indicate that scattering and the resulting elongated light path within the active layers have a stronger potential to increase the PSC device performances compared to reflected light reduction (Figure 3(a)).

The large  $J_{sc}$  enhancement when using microPDMS optical coatings resulted in a PCE increase from 6.75% for bare PNTz4T:PC<sub>71</sub>BM PSCs to 7.28% for the coated devices, respectively. According to Figure 3(c), when coated with microPDMS, the optical path lengths of light around 400, 490, 550 and 640 nm within the active layer are elongated by factors of 1.04, 1.06, 1.10 and 1.15, respectively. Note that the above elongations were calculated using simple geometry and without taking into account reflection at the active layer/metal electrode interface. The anti-reflective properties and the spatial redistribution of light when employing nanoPDMS or microPDMS at the glass/air interface of PSCs should also positively affect the device photovoltaic performances when the incident light is tilted with respect to the normal direction. In fact, the incident angle-dependent simulation results suggest that light scattering effects could lead

to a higher enhancement of the photocurrent when tilting the incident light up to 30 degrees (Table S1). The  $J$ - $V$  curves measured from the PNTz4T:PC<sub>71</sub>BM PSCs without PDMS and with microPDMS at incident angles varying from 0 to 30 degrees are presented in Figure 4(a).

These results clearly indicate that even when the incident light is tilted to an angle of 30 degrees, the strong light scattering and anti-reflective properties of microPDMS covered PSCs produces higher performances compared to the bare PSCs measured in optimal conditions (normal incident light). Flat PDMS coated PSCs also exhibit a superior angle dependent behavior than bare devices due to the higher impact of reflected light reduction at larger incidence angles. Although the performance reduction is smaller than for bare devices (Figure 4(b)), the  $J_{sc}$  value of flat PDMS coated PSCs also gradually decreases with increasing incidence angle. NanoPDMS coated PSCs display a flat PDMS-like trend for low angles up to 20 degrees but then switch to a microPDMS-like behavior at larger angles (Figure 4(b)). The stronger enhancement observed at high inclination angles for microPDMS with respect to nanoPDMS confirms that spatial light redistribution is more efficient when employing the quasi-random structures with high diameter dispersities present on the microPDMS surface.

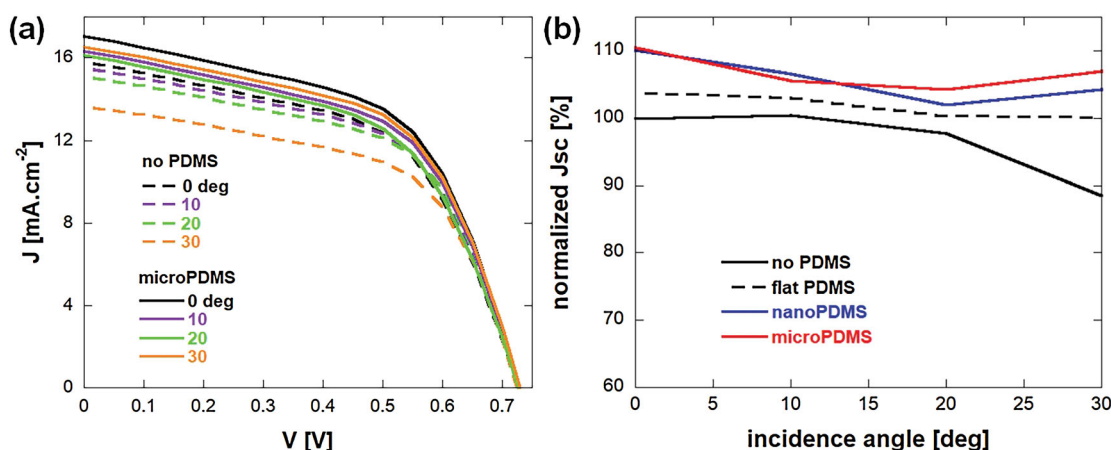


**Figure 4.** (a) J–V curves of bare and microPDMS-covered PNTz4T:PC<sub>71</sub>BM PSC measured for various light incident angles. (b) Incident angle-dependent normalized  $J_{sc}$  evolution of bare and PDMS-covered PNTz4T:PC<sub>71</sub>BM PSC.

## Conclusions

By using a combination of computational and experimental results, we have demonstrated that quasi-random structures fabricated using the low-cost polymer self-assembly approach can produce anti-reflective properties and strong light scattering to efficiently manipulate light into PSC active layers. When dome-like surfaces with dome diameter dispersities of 0.53 (microPDMS) and 0.43 (nanoPDMS) are placed at the glass/air interface of PNTz4T:PC<sub>71</sub>BM PSCs, they generate average  $J_{sc}$  increases of 7.9% and 6.2%, respectively. The stronger scattering ability of microPDMS resulted in a PCE increase from 6.75% to 7.28% compared to bare devices. Unlike the bare PSCs, when incident light is tilted up to 30 degrees, the performances of microPDMS-coated PSCs are not significantly reduced. Consequently, the facile fabrication method we introduce here could become a simple approach to efficiently harvest sunlight throughout the day using low-cost photovoltaic technologies.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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