Enhancement of the Power Conversion Efficiency of Organic Solar Cells by Surface Patterning of Azobenzene Thin Films

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Supporting Information

ABSTRACT: Nanoscale-patterned azobenzene thin films were incorporated in organic solar cells to scatter incident light, thus increasing the optical path length of photons inside the active area. This ultimately led to significant power conversion efficiency (PCE) enhancements in the active layer. Specifically, the azobenzene thin films were patterned with two-dimensional crossed surface relief gratings inscribed via laser interference lithography. The patterned films were then bleached and thermally stabilized by exposure to strong ultraviolet light before being incorporated in P3HT:PC61BM and PTB7:PC61BM solar cells. The fabricated solar cells exhibited a PCE enhancement of 133%, from 1.37 to 3.19%, for P3HT:PC61BM solar cells, and a PCE enhancement of 302%, from 0.53 to 2.13%, for PTB7:PC61BM solar cells.

1. INTRODUCTION

Consumption of fossil fuel has been rising exponentially since the beginning of the twentieth century. While it is possible that the reserves of fossil fuel will continue to grow as a result of continued exploration, the depletion of this source of energy is a lesser problem than the negative long-lasting effects resulting from its combustion. These include adverse consequences to human health and the threat of global climate change. These facts call for a greater emphasis on identifying and implementing alternative sources of energy such as solar energy. However, the performance of conventional inorganic solar cells has now reached a steady state with only minor improvements in the last 20 years. Some multijunction cells have progressed to PCE values beyond 30%; however, their cost is commercially not advantageous. Polymer organic solar cells offer many advantages compared to their inorganic counterparts, such as short energy payback times, low environmental impact during manufacturing, low cost and ease of fabrication, mechanical flexibility, and versatility of the chemical structure, but their relative low efficiency still limits their practical use and they have yet to reach the point of commercialization.

Organic polymer solar cells were developed in the 1980s and consisted of a single absorbing polymer sandwiched between two electrodes, resulting in efficiencies below 0.1%. The first pioneering work on polymer solar cells was the introduction by Tang in 1986 of a second organic layer, resulting in a bilayer cell with donor and acceptor layers that brought the efficiency to around 0.9%. The next breakthrough came with development by Yu et al. of a bulk-heterojunction structure by mixing soluble polymers and fullerenes to create a network of electron donor and acceptor materials. While early solar cells used poly[2-methoxy-5-(3,7-dimethylocxyloxy)-1,4-phenylenevinylene] (MDMO-PPV) as a polymer, the introduction of P3HT polymers saw an efficiency increase when used in conjunction with the fullerene PC61BM to around 4% due to a better absorption of visible light up to wavelengths of 650 nm. Recently, various polymers have been developed with increasing optical range, such as PTB7, which has an absorption range reaching 750 nm and was able to achieve a maximum efficiency of 9.2% when used with the fullerene PC71BM. However, due to low carrier mobility and short exciton lifetime, the internal quantum efficiency (IQE) of organic solar cells tends to decrease as the thickness of the...
active layer increases, thus organic solar cells need to remain in the thin-film form. This results in low light absorption limiting the efficiency of organic solar cells. Various approaches have been suggested to increase the optical absorption in thin-film organic solar cells, and these include tandem structures,⁹ plasmonic solar cells,¹⁰,¹¹ and ray-optical light trapping systems.¹²,¹³ An alternative method to improve light absorption in organic solar cells is to scatter incident light within the active layer of the solar cell, thus increasing the chance that photons would be absorbed and their energy be converted into electrical energy.

The theory of light scattering from nanostructures in solar cells¹⁴ was initially developed for conventional solar cells where the absorbing film is typically many light wavelengths thick. With an optically rough interface, the light propagation directions inside the material are randomized, thus resulting in a much longer propagation distance inside the active layer, and hence, a substantial absorption enhancement¹⁵,¹⁶ is obtained. This theory demonstrated that absorption enhancement could reach a maximum factor of $4n^2$, where $n$ is the refractive index of the active layer.¹⁴ By roughening both the active layer’s interfaces, an optical path length enhancement on the order of 50 times is theoretically possible, although in practice, enhancements of approximately 10 times have been reported in silicon solar cells.¹⁷ For thin films, some of the basic assumptions in the conventional scattering theory are not applicable, and an absorption enhancement factor of 48n² has been numerically demonstrated.¹⁸ Thus, there is a potential for substantial improvements in the efficiency of organic solar cells through light scattering. However, in practice, scattering by surface roughening is normally not used in organic solar cells as the surface roughness would exceed the film thickness. Instead, scattering is achieved in organic solar cells by doping one of the layers with metallic nanoparticles, such as silver and gold nanoparticles.¹⁹ Metallic nanowires,²⁰ nanocubes,²¹ nanoprism,s²² carbon nanotubes,²³−²⁵ and nanocomposites²⁶ have also been used for scattering light in thin-film organic solar cells. PCE enhancements of 16%²¹ and 14%²⁵ have been respectively reported for P3HT:PC₆₁BM and PTB7:[6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) solar cells with embedded nanoparticles. However, the size, shape, and density of the nanoparticles must be tuned to the chosen active materials, and the efficiency enhancements are often limited to a narrow spectral range, typically around 100 nm. In this work, a different approach is explored by incorporating nano-patterned azobenzene thin films in organic solar cells to scatter incident light before entering the solar cell active area.

![Figure 1](image-url)
The photoinduced fabrication of nanostructures in azobenzene polymer thin films was first reported by Rochon et al.\(^7\) in the form of surface relief gratings (SRGs). They noted that the azobenzene chromophore underwent a *trans*-<em>cis</em>-*trans* photoisomerization when exposed to a laser light with a wavelength in the polymer's absorption region and that SRGs could be inscribed in a single-step process using interference lithography. The optical inscription of diffraction gratings in azobenzene materials is a single-step and inexpensive process that can be accomplish in only a few minutes using a laser with cheap optics. The resulting nanostructures are stable over time spanning decades, and they can be coated with other materials, depending on the application. While azobenzene is a popular material nowadays for the optical inscription of SRGs, as well as many other applications,\(^8\) it has a strong absorption in the visible spectrum below 600 nm.\(^9\) Furthermore, azobenzene nanostructures collapse when heated above their glass transition temperature, typically around 80 °C.\(^10\) These drawbacks limit azobenzene applications in solar cells as not only would the transmission of light be negatively affected but also the nanostructures could be destroyed during high-temperature annealing, which is often required in the manufacturing of organic solar cells, notably the P3HT:PC\(_{61}\)BM heterojunction blend.\(^4\) However, an increased transmission of azobenzene films in the visible range and thermal stability have been reported after exposure to strong ultraviolet (UV) light.\(^29,31,32\) One example was found in the literature using UV-treated azobenzene surface relief gratings as scattering centers to improve light emission from organic light-emitting diodes (OLEDs).\(^33\) However, a literature review did not reveal any published reports on using nanopatterned and bleached azobenzene films to enhance the efficiency of solar cells. In this work, azobenzene thin films were patterned with crossed surface relief gratings fabricated by laser interference lithography and bleached by prolonged exposure to strong UV light. P3HT:PC\(_{61}\)BM and PTB7:PC\(_{61}\)BM solar cells were then fabricated with transparent bottom electrodes on the opposing side of the glass substrates from where the azobenzene films are located, a design referred to as double-sided solar cells for the rest of this work. The solar cells with the patterned and bleached azobenzene thin films showed significant enhancements in the current density \(J_{sc}\) and the PCE compared to the control solar cells. Furthermore, the patterned azobenzene thin films can be used with different active materials or solar cell architectures without requiring a redesign, thus providing a versatile option compatible with mass production.

2. RESULTS

2.1. Effect of the UV Exposure on the Transmission of the Azobenzene Thin Films. Amorphous azobenzene thin films were bleached by a strong UV light exposure at a distance of 3.5 cm from the lamp. The transmission of the bleached amorphous azobenzene thin films was taken at different exposure times, and it was found to saturate after 20 h of exposure, as shown in Figure 1a. In this figure, there are two peaks in the spectrum changing over time, one near 300 nm and the other near 490 nm. The behavior of the first peak corresponds to the reversible *trans*–*cis* isomerization process, which first gets stronger and then decreases as more and more
molecules are damaged from continued photoexposure, while the second peak is associated with an irreversible photo-degradation. The transmission of the azobenzene thin films was found to also depend on the distance of the sample from the lamp, as shown in Figure 1b, with better transmission associated with a closer distance to the lamp. A transmission value of 75% at a wavelength of 450 nm was recorded for an amorphous azobenzene thin film at a distance of 3.5 cm to the UV lamp, while a transmission value of only 37% at a wavelength of 450 nm was recorded for a sample positioned at 6 cm from the lamp. In contrast, an unbleached amorphous azobenzene thin film has a transmission of only 3% at the same wavelength. Figure 1c,d is photographs of an azobenzene thin film before and after a 20 h UV exposure at a 3.5 cm distance from the lamp, respectively. A dip in transmission can be seen in Figure 1b in the 600–750 nm range for an unbleached azobenzene thin film patterned with crossed gratings with a pitch of \( \Lambda = 450 \) nm. This is most likely the result of incident light being coupled in the azobenzene layer. However, this dip disappears for UV-treated films since the UV exposure also results in a modification of the surface profile of the patterned azobenzene thin films, making them more suitable for scattering than diffraction.

2.2. Effects of UV Exposure on the Nanostructures of the Azobenzene Thin Films. The UV exposure had several effects on the nanostructures of the azobenzene thin films. The first effect was the partial destruction of the original crossed SRGs, with grating modulation depths decreasing to a range between 5 and 20 nm for bleached samples, compared to the original grating modulation depths of \( \sim 85 \) nm, as seen in Figure 2. The grating modulation depth for the bleached films was found to depend on the distance from the sample to the UV lamp, which was varied from 3.5 to 6 cm at a constant 20 h exposure, with better preservation of the grating profiles associated with shorter exposure distances. The second effect is the apparition of volcano-shaped nanostructures. It was also found that the lamp distance had a critical effect on the size of these nanostructures, with maximum heights varying between 34 nm at a sample–lamp distance of 6 cm and 287 nm at a sample–lamp distance of 3.5 cm. The impact of the UV lamp distance on the azobenzene nanostructures of the azobenzene thin films is discussed in further details in the Supporting Information.

As the gratings are better preserved at shorter lamp-sample distances, their partial destruction cannot be due to the sample heating above the glass transition temperature of the azobenzene film under the UV lamp. It is more likely that the initial absorption of the UV energy allows the azobenzene chromophore to undergo a \( \text{trans} \rightarrow \text{cis} \) isomerization responsible for the partial destruction of the grating, but the high intensity of the UV light causes an irreversible photodegradation of the azobenzene molecules, “freezing” the molecules in place. As the light would be more intense for a sample closer to the source, the photodegradation would be more rapid, therefore freezing the molecules in place at a faster rate. One possible explanation for the formation of the volcano-shaped nanostructures is that the UV irradiation produces photo-induced surface reorientation and mass movement of the azobenzene molecules. This would create surface defects, which in turn would act as seeds for spontaneous surface relief gratings (SSRGs).\(^{34}\) Crossed gratings are normally associated with diffraction instead of scattering. However, the UV treatment of the crossed gratings resulted in partial destruction of the gratings, with only a minimal modulation depth remaining. Combined with the apparition of the volcano-shaped nanostructures, the results are rougher surfaces, which are appropriate for scattering light.

2.3. Thermal Stability of UV-Treated Azobenzene Thin Films. The irreversible photodegradation of the azobenzene molecules was also found to increase their thermal stability, as the degraded molecules would not be able to undergo a \( \text{cis-} \rightarrow \text{trans} \) isomerization. Before fabricating the organic thin-film solar cells on the opposing side of the substrate, the thermal stability of the UV-treated gratings was verified. In Figure 3a,b, it can be seen that heating an unbleached azobenzene molecular glass thin film above its 71 °C glass transition temperature\(^{35}\) results in total erasure of the crossed gratings by allowing the azobenzene chromophores to relax back to their \( \text{trans} \) isomers.\(^{36}\) However, as shown in Figure 3c,d, a 20 h UV treatment resulted in thermal stability of the nanostructures, with the \( \text{rms} \) roughness and maximum height of the nanostructures \( R_q/R_{\text{rms}} \) of the film measured at 4.6/53 nm before heating and 5.1/57 nm after heating. While the thermal stability of UV-treated azobenzene structures has been previously observed for maleimide-based copolymers bearing azobenzene moieties, a copolymer of 4’-[2- (methacryloyloxy)ethyl] ethylamino]-4-nitroazobenzene with 2 methacryloyloxy-phenol (polyDR1M),\(^{37}\) and an amorphous polymer containing Disperse Red 1 (DR1) and cross-linkable acrylic groups as separate side groups,\(^{40}\) this thermal stability effect has never been reported for the newer gDR1 compound used in this work.

3. DISCUSSIONS

As seen earlier in Figure 1, the bleached azobenzene thin films still absorbed some light in the visible range even after a prolonged 20 h UV exposure. The absorbance spectrum of the P3HT:PC\textsubscript{61}BM blend thin film largely overlaps with the absorbance spectrum of the gDR1 thin film, as shown in Figure 4a. The wavelength range of 350–600 nm contains approximately 90% of the gDR1 thin-film absorbance spectrum, while P3HT:PC\textsubscript{61}BM has 81% of its absorbance in
Solar cells made from this blend would therefore be largely affected by the transmission of the azobenzene thin films. This issue could be subsidiary in a polymer/fullerene blend less susceptible to the azobenzene absorbance. For example, PTB7:PC61BM only has 51% of its absorbance in the 350−600 nm range. Double-sided PTB7:PC61BM solar cells with patterned and UV-treated azobenzene thin films are therefore expected to have stronger PCE enhancements, compared to a control solar cell, than P3HT:PC61BM solar cells with similar roughness, nanostructure maximum heights, and transmission of the azobenzene thin film. The J−V characteristics of double-sided P3HT:PC61BM and PTB7:PC61BM solar cells with different Rs/Rqmax values are shown in (c) and (d), respectively.

Control P3HT:PC61BM solar cells without the azobenzene layer as well as double-sided P3HT:PC61BM solar cells with patterned and bleached azobenzene thin films were fabricated as per the procedures detailed in the Experimental Method section. One sample containing four solar cells was patterned uniquely by the volcano-shaped nanostructures resulting from the UV exposure. This resulted in a roughness and maximum height of the nanostructures Rq/Rqmax = 2.1/40 nm. In all other cases, crossed gratings were first inscribed on the azobenzene films, and then the UV lamp−sample distance was varied from 5 cm, resulting in azobenzene thin films with Rq/Rqmax = 3.9/41 nm, to 3.5 cm, resulting in Rq/Rqmax = 14/136 nm. The current−voltage J−V characteristic curves for the best P3HT:PC61BM solar cells obtained for each of the Rq/Rqmax values are shown in Figure 4c. Control PTB7:PC61BM solar cells and double-sided PTB7:PC61BM solar cells with azobenzene thin films patterned by UV exposure only (Rq/Rqmax = 3.6/52 nm) or a combination of crossed gratings and UV exposure (Rq/Rqmax = 3.4/34 nm, 9.0/80 nm, and 36/287 nm) were also fabricated as per the procedures detailed in the Experimental Method section using varied UV lamp−sample
distances. The $J$–$V$ characteristic curves for the best PTB7:PC61BM solar cells obtained for each of the $R_q/R_{\text{rms}}$ values are shown in Figure 4d.

The first point of interest in Figure 4b is the $J$–$V$ characteristics of the P3HT: PC61BM solar cell with $R_q/R_{\text{rms}} = 2.1/40$ nm obtained by patterning the azobenzene thin film by UV exposure only. The solar cells from this sample exhibited an average PCE of 1.0 ± 0.6% with the best solar cell having a $J_{\text{sc}}$ of 13.49 mA/cm$^2$, a $V_{\text{oc}}$ of 0.58 V, an FF of 0.19, and an efficiency of 1.47%, up from 1.37% for the best P3HT:PC61BM control solar cell (average of 0.90 ± 0.06%).

With both the average and the best solar cell efficiencies surpassing those of the control solar cell, the PCE enhancements are most likely attributed to scattering from the volcano-shaped nanostructures formed during UV exposure. Since the azobenzene thin film still absorbed some light even after 20 h of bleaching, a lower PCE would be expected from solar cells made with an amorphous layer of bleached azobenzene compared to a control solar cell made without the azobenzene layer. The increase in the efficiency of the solar cell with $R_q/R_{\text{rms}} = 2.1/40$ nm can therefore only be attributed to the scattering of incident light by the azobenzene volcano-shaped nanostructures resulting from the UV exposure, with the scattering effect slightly overcompensating for the loss in transmission.

To further increase the surface roughness of the azobenzene layer, crossed gratings were first inscribed on the surface of the azobenzene films prior to the UV exposure. The double-sided P3HT:PC61BM solar cells with crossed gratings and an $R_q/R_{\text{rms}} = 3.9/41$ nm had an increase average PCE of 2 ± 1% (compared to 0.9 ± 0.4% for the control solar cells). The best solar cell with this design had a high $J_{\text{sc}}$ of 23.68 mA/cm$^2$ compared to 13.62 mA/cm$^2$ for the best control solar cell, a strong indication of successful scattering within the solar cell leading to an increased absorption of the light. It also exhibited an improved $V_{\text{oc}}$ of 0.59 V, an FF of 0.23, and an efficiency of 3.19%, up from 1.37% for the best control solar cell, a significant efficiency enhancement of 133%. However, a further increase in $R_{\text{rms}}$ with $R_q/R_{\text{rms}} = 14/136$ nm, resulted in a smaller increase in $J_{\text{sc}}$ of 19.89 mA/cm$^2$, a $V_{\text{oc}}$ of 0.58 V, an FF of 0.19, and a PCE of 2.32%. This effect is probably due to a non-optimized forward/total scattering ratio. The best solar cell with a nanostructure size of 80 nm had an efficiency of 1.56%, while the best solar cell with the nanostructure size of 287 nm had an efficiency of 1.39%. Table 1 summarizes the $J$–$V$ characteristics of the solar cells fabricated during this work.

### Table 1. Summary of the $J$–$V$ Characteristics of the Double-Sided Solar Cells

| design                  | best $J_{\text{sc}}$ (mA/cm$^2$) | best $V_{\text{oc}}$(V) | best FF | best PCE (%) |
|-------------------------|---------------------------------|-------------------------|--------|--------------|
| Double-sided P3HT:PC61BM solar cells |                                 |                         |        |              |
| control                | 13.62                           | 0.54                    | 0.18   | 1.37         |
| $R_q/R_{\text{rms}}$ = 2.1/40 nm | 13.49                           | 0.58                    | 0.19   | 1.47         |
| $R_q/R_{\text{rms}}$ = 3.9/41 nm | 23.68                           | 0.59                    | 0.23   | 3.19         |
| $R_q/R_{\text{rms}}$ = 14/136 nm | 19.89                           | 0.58                    | 0.19   | 2.32         |
| Double-sided PTB7:PC61BM solar cells |                                 |                         |        |              |
| control                | 5.24                            | 0.49                    | 0.21   | 0.53         |
| $R_q/R_{\text{rms}}$ = 3.4/34 nm | 10.14                           | 0.64                    | 0.22   | 1.74         |
| $R_q/R_{\text{rms}}$ = 3.6/52 nm | 13.93                           | 0.69                    | 0.22   | 2.13         |
| $R_q/R_{\text{rms}}$ = 90/80 nm | 13.09                           | 0.60                    | 0.20   | 1.56         |
| $R_q/R_{\text{rms}}$ = 36/287 nm | 12.00                           | 0.69                    | 0.17   | 1.39         |

Figure 5 shows the enhancements of the $J_{\text{sc}}$, $V_{\text{oc}}$, FF, and PCE of the P3HT:PC61BM and PTB7:PC61BM solar cells for different values of $\text{rms}$ roughness $R_q$ and maximum height $R_{\text{rms}}$ values of the nanostructures of the azobenzene thin films. As it can be seen from this graph, in both P3HT:PC61BM and PTB7:PC61BM solar cells, the scattering of the photons by the azobenzene nanostructures mainly resulted in an improved $J_{\text{sc}}$ and PCE, with optimal values achieved with increased $\text{rms}$ roughness of the azobenzene thin films as long as the maximum heights of the azobenzene nanostructures remained below ~60 nm. Stronger enhancements were achieved with PTB7:PC61BM solar cells as PTB7 is less affected by the azobenzene absorption than P3HT due to a different absorbance spectrum. Furthermore, it can be noted that the strongest enhancements were achieved using similar roughness values for P3HT:PC61BM and PTB7:PC61BM solar cells, showing the versatility of the double-sided solar cell design with patterned and bleached azobenzene thin films. Once the
were achieved using a similar azobenzene nanostructure.

The UV exposure of the patterned azobenzene thin films resulted in the partial destruction of the crossed gratings due to the initial absorption of the UV energy by the azobenzene molecules, the formation of volcano-shaped nanostructures and, finally, an enhanced thermal stability of the inscribed gratings well beyond the glass transition temperature of the azobenzene film. For the fabricated solar cells, the increase in the optical path length of the incident photons within the active layer, due to scattering, resulted in significant $J_{sc}$ enhancements, which are a strong indication of improved absorption, which in turn led to PCE enhancements. Larger PCE enhancements were achieved in the fabricated solar cells with increased $R_{q,rms}$ roughness of the azobenzene thin films, however the heights of the resulting nanostructures needed to be carefully controlled to optimize the ratio of forward/total scattering.

Figure 5. Enhancements of the solar cells characteristics of (a) P3HT:PC$_6$BM and (b) PTB7:PC$_6$BM solar cells after the incorporation of azobenzene thin films patterned by crossed gratings and UV exposure. An improved $J_{sc}$ and PCE are observed, with optimal values achieved with increased $R_{q,rms}$ the $R_{q,rms}$ roughness of the azobenzene nano film, as long as the maximum height of the azobenzene nanostructures, $R_{max}$, remained $<$40–60 nm.

5. EXPERIMENTAL METHODS

5.1. Substrate and Solutions Preparations. Soda lime glass slides (no. 2947) (Corning Glass Works, Corning, USA) were cut to dimensions 3.4 cm × 2.5 cm and were cleaned with a liquid dish soap followed by a series of ultrasonic baths of detergent water, acetone, isopropanol, and deionized water for 10 min each, with deionized water rinse between each bath. The slides were then kept in deionized water until used. Immediately prior to use, the glass slides were dried in an oven at 120 °C for 15 min and blow-dried with nitrogen to remove any dust particles. Solutions of Disperse Red 1 molecular glass (gDR1), which are made of azobenzene chromophores functionalized with methylaminotriazine backbones, were prepared by dissolving 0.18 g of gDR1 in 5.82 g of dichloromethane (DCM) and shaking the mixture in a mechanical shaker for 1 h to obtain a 3% wt solution, which yielded 400 nm thick films when spin-coated at 1000 rpm. A highly conductive formulation of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PE-DOT:PS), namely, Heraeus Clevios PH1000 (Ossila, Sheffield, England), was mixed with dimethyl sulfoxide (DMSO) for an hour in a mechanical shaker to obtain a 5% wt solution, with a conductivity of 677.69 S/cm for a thin film with a thickness of 105 nm. The active layer consisted of either P3HT:PC$_6$BM or PTB7:PC$_6$BM polymer/fullerene heterojunction blends. The polymers P3HT (SOL4106, molecular weight (Mw) 50–70 kilodaltons (KDa)), PTB7 (SOL4700M, Mw 50–100 KDa), and fullerene PC$_6$BM (SOLS061) were acquired from Solaris Chem Inc., Montreal, Canada. Solutions of P3HT:PC$_6$BM were prepared by first mixing 0.093 g of P3HT in 2 mL of chlorobenzene (CB) and 0.074 g of PC$_6$BM in 2 mL of CB inside a nitrogen-filled glovebox. Once sealed and wrapped in an aluminum foil, the vials were transferred to a mechanical shaker and shaken overnight. The prepared solutions were placed in an ultrasonic bath for 1 h to ensure complete dissolution. The vials were then transferred back to the glovebox, and the solutions were mixed to form P3HT:PC$_6$BM (1:0.8) 25 mg/mL in CB solution, which was shaken again in a mechanical shaker for 1 h. A similar procedure was conducted to prepare the PTB7:PC$_6$BM solutions: 0.040 g of PTB7 and 0.080 g of PC$_6$BM in 4 mL of CB were mixed to obtain PTB7:PC$_6$BM (1:2) 30 mg/mL in CB solution. Finally, the solutions were filtered with a 0.45 μm syringe filter prior to each use.

5.2. Inscription of Surface Relief Gratings on Azobenzene Thin Films. Thin films of azobenzene were prepared by spin-coating 60 μL of the gDR1 solution at 1000 rpm for 20 s using a Headway Research spin-coater (Garland, USA). The cast films were cured in an oven at 95 °C for 30 min, producing films with a thickness range between 150 and 200 nm, as measured by a Sloan Dektak IIA/IID profilometer.

ratio of forward/total scattering is optimized, there is no need for redesign of the scattering films to accommodate different active materials or solar cell architectures.

4. CONCLUSIONS

In this work, Disperse Red 1 azobenzene molecular glass thin films were patterned by crossed surface relief gratings via laser interference lithography, and then they were bleached upon exposure to a strong UV light for 20 h to increase their transparency. The resulting films were used as scattering centers in double-sided design organic thin film solar cells with the active layer being either P3HT:PC$_6$BM or PTB7:PC$_6$BM. The UV exposure of the patterned azobenzene thin films resulted in the partial destruction of the crossed gratings due to the initial absorption of the UV energy by the azobenzene molecules, the formation of volcano-shaped nanostructures and, finally, an enhanced thermal stability of the inscribed gratings well beyond the glass transition temperature of the azobenzene film. For the fabricated solar cells, the increase in the optical path length of the incident photons within the active layer, due to scattering, resulted in significant $J_{sc}$ enhancements, which are a strong indication of improved absorption, which in turn led to PCE enhancements. Larger PCE enhancements were achieved in the fabricated solar cells with increased $R_{q,rms}$ roughness of the azobenzene thin films, however the heights of the resulting nanostructures needed to be carefully controlled to optimize the ratio of forward/total scattering. The best P3HT:PC$_6$BM solar cell with a nanopatterned and bleached azobenzene thin film exhibited a high $J_{sc}$ of 23.68 mA/cm$^2$ compared to 13.62 mA/cm$^2$ for a control solar cell, an enhanced PCE of 3.19%, and a significant PCE enhancement of 133%. The best PTB7:PC$_6$BM solar cell, also with a nanopatterned and bleached azobenzene film, exhibited a $J_{sc}$ of 13.97 mA/cm$^2$ compared to 5.24 mA/cm$^2$ for the control solar cell and an PCE of 2.13%, a PCE enhancement of 302%. The strongest PCE enhancements were achieved using a similar azobenzene nanostructure.
Santa Barbara, USA), with a root-mean-squared (\(\text{rms}\)) roughness \(R_q = 0.5\) nm and a maximum profile height \(R_{q_{\text{max}}} = 3.0\) nm, as measured by a Bruker dimension edge atomic force microscope (AFM) (Santa Barbara, USA). The AFM tip scanned the surface using a peak-force tapping mode, on a \(5 \times 5\) \(\mu\)m area, with a scan rate of 1 Hz per line. The collected images were then corrected and fitted by a built-in 2D plane fit function in the AFM software, which was also used to obtain the average roughness over the entire scanned area. The films were then patterned using laser interference lithography to form crossed surface relief gratings, as depicted in Figure 6. The beam from a Coherent Verdi V5 diode-pumped continuous wave laser (Santa Clara, USA) with a wavelength of 532 nm and an irradiance of 416 mW/cm\(^2\) was passed through a 25 \(\mu\)m spatial filter to reduce its Gaussian profile. The beam was then collimated using a plano-convex lens, and it was circularly polarized with a quarter-wave plate. A variable iris was used to control the diameter of the laser beam incident on a Lloyd’s mirror interferometer, which consisted of a mirror and sample holder fastened at a 90° angle and mounted on a rotating platform. The platform was remotely controlled by a LabView program and a Velmex (Bloomfield, USA) stepping motor controller, which enabled the adjustment of the laser incidence angle, thus allowing control of the grating spacing. The intersection axis between the mirror and sample holder was positioned at the center of the laser beam so that the half of the laser beam was incident on the mirror’s surface and the other half on the sample’s surface to create an interference pattern. The grating spacing was arbitrarily set to \(\Lambda = 450\) nm for all gratings in this work. A gratings was first inscribed with a laser exposure time of 120 s, followed by a 90° rotation of the sample with respect to the vertical plane, and a second grating was inscribed on the same area with an exposure time of only 55 s. This procedure resulted in the fabrication of a two-dimensional crossed grating with an approximate 85 nm modulation depth along the first grating vector and 60 nm along the second grating vector.

As azobenzene has a strong absorption in the visible range, the films were made transparent, or bleached, by a prolonged 20 h UV exposure using an ORC HmW-6238 mercury lamp (Torrance, USA). No optical components such as filters or lenses were used between the lamp and the sample, and the distance of the samples to the UV lamp was varied between 3.5 and 6 cm, resulting in a lamp irradiance between 7.4 and 2.5 kW/m\(^2\), respectively.

5.3. Incorporation of Patterned Azobenzene Films in Solar Cells. Organic thin-film polymer solar cells were built in a direct structure configuration on the opposing side of the glass substrate from where the azobenzene nanostructures were formed, as depicted in Figure 7a. To prevent damage to the azobenzene nanostructures while fabricating the solar cell, a second glass slide was temporarily fixed over the azobenzene film with a small gap in between the two slides. Silver conductive paste was then applied to select areas of the glass slide surface where the solar cell would be built to improve the anode and cathode electrode contact points and the entire device was cured in an oven at 120 °C for 20 min. A single thin-film anode made of the PH1000 + DMSO mixture was spin-coated over the dried silver paste inside a nitrogen-filled glovebox at 2800 rpm for 60 s. The cathode silver paste
contacts and the edges of the substrate were cleaned with deionized water to remove the excess PH1000 + DMSO solution, and the sample was annealed at 120 °C for 10 min under N2 atmosphere, producing a bottom electrode with a thickness of ~100 nm. For the P3HT:PC61BM solar cells, 120 μL of P3HT:PC61BM (1:0.8), 25 mg/mL in CB, was spin-coated inside a nitrogen-filled glovebox at 1100 rpm for 30 s. The anode and cathode silver paste contacts were cleaned with CB, and the sample was annealed at 120 °C for 30 min under N2, producing an active layer thickness of ~90 nm. For PTB7:PC61BM, 120 μL of PTB7:PC61BM (1:2), 30 mg/mL in CB, was spin-coated inside a nitrogen-filled glovebox at 1100 rpm for 30 s. Similarly, the anode and cathode silver paste contacts were cleaned with CB, and the sample was left to dry uncovered in a nitrogen-filled glovebox for 2 h in the dark. The additional glass slide used to protect the azobenzene nanostructures during the fabrication of the solar cell was then removed. Finally, the solar cell fabrication was completed by evaporating a 100 nm thick layer of aluminum using a Key High Vacuum Products KV-301 (Nesconset, USA) physical vapor evaporator controlled by a Varian Turbo-V 301 AG vacuum controller (Santa Clara, USA) through an in-house built evaporation mask. The aluminum deposition rate was kept between 3 and 5 Å/s, as measured using a Sigma Instrument SQM-160 rate/thickness monitor (Bad Ragaz, Switzerland). The overlap of the electrodes resulted in four solar cells per sample with active areas of 8.49 mm2, as illustrated in Figure 7b.

The standard spectrum for measuring terrestrial solar cell efficiency is AM1.5G, which is available in ASTM G-173-03(2006). The AM1.5G spectrum represents the total power per unit area that is received at the surface of the Earth at a solar zenith angle of 48.2° on a clear sunny day. The integral of this spectrum over the entire spectrum is the input power Pmax used in the calculation of solar cells PCE and has a value of 1000 W/m2. This has become the standard irradiance at which the efficiencies of solar cells are reported and is often referred to as 1 Sun condition. The solar cells fabricated for this work were tested using an in-house built solar simulator composed of an Oriel 66058 xenon arc lamp (Irvine, USA) powered by an Oriel 200 W power supply (Irvine, USA). To reduce the strong emissions of the xenon arc lamp in the infrared region and to achieve a closer spectral match to the standard AM1.5G spectrum, the lamp was paired with an Omega Optical AM1.5G filter (Brattleboro, USA). To get the standard 1 Sun illumination testing condition, a Scientech 362 power energy meter (London, Canada) equipped with a Scientech 380101 silicon detector (London, Canada) was used to determine the required distance between the sample and the xenon arc lamp. Even though the PCE is measured as a ratio of the maximum output power from the solar cell to the input power, respecting the 1 Sun standard test condition is important as, at low light levels, the effect of the shunt resistance of the solar cell becomes increasingly important, and therefore, standardization of the input light intensity for testing and reporting purposes is required. However, due to the spectral responsivity of the silicon detector, care was taken during the calibration of the solar simulator to avoid overestimation of the efficiency. The chosen silicon detector can detect in the wavelength range of 280–1064 nm. This range contains 78.4% of the AM1.5G spectrum or a total irradiance of 784 W/m2. Using E = P

\[ P_{\text{nom}} = \frac{V_{\text{oc}} \times FF}{P_{\text{in}} \times \text{active Area}} \]  

and

\[ FF = \frac{J_{\text{mp}} V_{\text{mp}}}{J_{\text{sc}} V_{\text{oc}}} \]

where \( P_{\text{nom}} = J_{\text{mp}} V_{\text{mp}} \) is the point of the maximum output power from the solar cell.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02844.

Impact of UV lamp distance on the nanostructures of the azobenzene thin films (PDF)

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**Notes**

The authors declare no competing financial interest.

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