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Disordered polymer anti-reflective coating for improved perovskite photovoltaics

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Abstract

Light management through low index medium, such as anti-reflective coating (ARC) provides practical solution to improve the efficiency of photovoltaics. However, a brute-force development of photonic structure on ARC is not necessarily useful, because of random scattering associated to impediment of light transmission. Here, we leverage the concept of disorder- rather than random-structured on ARC for improving efficiency without modifying original architecture of thin-film photovoltaics. We demonstrate a disordered polymer that leads to a total reflectance of 5 % while demonstrating a high transmission of 94 % across 300 to 820 nm wavelength. Next, we find that the arrangement of disordered points and line arrays constructing the polymer is the key to control bandwidth performance of the ARC. Finally, we apply this into $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite, and through experiments with wave-optics and full-device simulation showing 1.6-fold absorption gain leading to 19.59 % power-conversion-efficiency by the presence of disordered ARC.

Keywords: disorders, polymers, anti-reflective coatings, halide perovskites, photovoltaics

An anti-reflective coating (ARC) serves to reduce reflectance losses and is a very important element widely applied for improving energy efficiency of mobile phone display and solar cell technologies.¹⁻⁴ It is the last interface connecting optoelectronic devices with additional photonic environment which allows light to enter or escape, therefore, it serves as a practical platform for light-management strategies without having to modify the original electronic device properties. Typically, it is in a form of flat or patterned dielectric layer (sub-micron thick) having an effective optical impedance ranging in between free space (air) and active materials inside the devices.⁵ In the classical ray optics, engineering the thickness and optical index of the ARC is the key to minimize the total (Fresnel) reflection losses through destructive interfering all reflection coefficients at all polarization and angle of incidence.⁶ However, both flat and periodically patterned ARCs work efficiently well at one polarization state, and limited to narrow-incident angle and/or spectral bandwidth.⁷ In contrast, for high efficiency solar panels, it is necessary to have wide-incident angle and broadband spectral response against unpolarized light source. This is particularly the case for solar panels at terrestrial conditions (cloudy weather, change in light intensity, and diffused sunlight).⁴⁻⁸

Patterning an optically flat-ARC have been exclusively studied for example using micro-pyramid textures,⁷ micro-lens arrays,⁹ nanopillar-arrays,³ and micro/nanoporous inclusions.¹⁰ Such varieties have shown to enhance optical excitation modes useful for light-trapping in solar cells. Albeit powerful to reduce the total reflectance and increase absorption in the underlying high-index active materials,^{11,12} patterning low-index materials usually comes at the cost of reducing total transmittance associated with scattering losses, thereby no longer efficient as ARC. On top of that, controlling in-plane light propagation within low-index ARC materials is rather counter intuitive, a brute-force approach on surface patterning in low-index ARC is not necessarily useful for improving light in-coupling for solar cells.⁸ Ideally, patterning ARC should significantly reduce its total reflectance without sacrificing the total transmission; even a small defect on ARC may induce scattering losses, hence reducing light transmission. Conversely, a structural correlation of disorder patterns on ARC offers reliable solution to circumvent the aforementioned problems owing to its known broadband spectra and angular response, and much higher degree of

freedom to control optical excitation through directional light scattering,¹³ photon localization,¹⁴ and disordered hyperuniformity.^{15,16}

ARC made by polymer materials such as polydimethylsiloxane (PDMS) offers structural flexibility to mold the shape, arrangement, and dimensional features of the patterns;¹⁷ all of these are the basic playgrounds required to achieve the goal of reducing total reflectance and maintaining/inducing high optical transmission. Furthermore, solution processed polymer provides unlimited parameter spaces (compared to vacuum processed-ARCs) to modify its optical response/aggregate such as effective index, directional emission, or even phosphorous inclusion matrix for down-/up-conversion process, thus makes it an excellent platform for light management ARC. Particularly, micro-pyramid textures made by PDMS is an interesting platform to study the effect of structural arrangement, correlation, and complex light propagation through low-index contrast ARC. This platform is easy to prepare using a simple curing process of polymer on a pre-patterned silicon master, and have been widely applied in a variety of solar cell technologies such as CdTe,¹⁸ Organic,⁸ CIGS,¹⁹ InGaP/GaAs/Ge,¹⁰ Si,²⁰ and perovskites,²¹ to improve power conversion efficiency without the need to modify the device architecture. Given its benefit and ease of integration into the existing devices, it is imperative to carefully assess the role of each parameter and realize where the potentials are of polymer as a robust and reliable ARC.

Here, we leverage the concept of disorder-, rather than random-structures, on micro-pyramid PDMS polymer to study the optical transport of efficient anti-reflective coating that is useful for perovskite solar cells. Although the dielectric contrast of this PDMS is low, a strong photonic effect can be observed in such disorder structure.¹⁶ Using a set of optical measurements and coupled wave-optics with full device simulation, we demonstrate the importance of structural disorder to reduce the total reflectance below 5 % while maintaining high transmission above 94 % which indicates successful ARC. We apply this concept in one of state-of-the-art perovskite solar cells and show 1.6-fold absorption enhancement. This gives rise to 19.59 % power-conversion-efficiency while maintaining the electrical properties of the device relatively unchanged (open-circuit voltage and fill-factor). Interestingly, the disorder of the polymer ARC appears translucent to white which may signify a diffused light-coupling taking place over a broadband spectrum. Such properties are highly relevant to maintain high efficiency of perovskite solar panels for terrestrial condition (cloudy weather and light intensity fluctuation over time).

We began by fabricating the disordered polymer ARC by a standard replication method of patterned PDMS using a pre-textured Si master containing disordered patterns. Briefly, a hard PDMS precursor was spin-coated on the pre-textured Si master, and after curing followed by a drop-casting a soft PDMS precursor. After fully cured, the combined hard-soft PDMS can be detached easily from the Si master to produce an ARC having around 0.5 to 2 microns features of disordered pyramid surfaces with 100 % filling-fraction. **Figure 1a** illustrates a three-dimensional reconstruction of the ARC based on the actual surface morphology obtained from scanning electron microscopy (SEM) image (**Figure S1**). The effect of curing method, surface defect, ARC thickness, characteristic angle and arrangement of the pyramidal surfaces is discussed in the supplementary information (**Figure S2-S5**). **Figure 1b** shows the translucency of ARC surface having disordered pyramidal structures, and compared to the flat version of identical PDMS ARC and quartz. The digital “9” red-LED image is somewhat hidden behind the disordered ARC that qualitatively suggests reduced reflection. Increasing focal distance between the disordered ARC and object makes the disordered surface appeared white all the way toward the edges (**Figure 1c**). Here, a long photon diffusion over 30 mm of the lateral sample size (much larger than the ARC base thickness) may take place due to multiple photon scattering propagating through the disordered medium.¹⁴ Such scattering is generally seen as an impediment for light transmission if its mean free path is shorter than the ARC thickness. In translucent medium, such photon diffusion can be scaled with its transmission,²² and this gives us over 150 mm of scattering mean free path. Structural correlation of the disordered micro-pyramids plays an important role in determining the mean free path of such photon diffusion, whereas the base PDMS thickness does not (**Figure S6**).

To quantify the reflection and transmission losses, we measured the total reflection and transmission of the disordered ARC whose spectra were collected over 300 to 1200 nm wavelength at all direction using an integrating sphere monitored by UV-Vis-NIR spectrometer. Reflectance of silver mirror (Thorlabs, PFSQ20-03-P01) and transmission of magnesium fluoride windows (Thorlabs, WG61059) were used as reference samples to normalize the experimentally obtained reflectance and transmission data in order to eliminate any discrepancy from measurement errors. In the case of disordered sample, the broadband reflectance reduces to ~ 5 % against ~7 and 8 % for the case of flat and quartz samples, respectively (**Figure 1d**). The reduction in total reflectance on disordered sample did not compromise its total transmittance up to 820 nm wavelength. Interestingly, the total transmittance on disordered sample (~ 94 %) is even higher than flat or

quartz sample (~92 %) from 300 nm to 620 nm wavelength (**Figure 1e**). The transmission cut-off appears above 820 nm wavelength for disordered sample, but not found for flat sample and quartz (**Figure S7**). Using steady-state photoluminescence and time-resolved photoluminescence lifetime, we probed two contrasting emitters of CdSe and PbS quantum dots that emits below and above this 820 nm transmission cut-off. From the emission spectra and transient decay of these quantum dots after filtering by the disordered sample, it seems that a photonic bandgap may form within the disordered sample, but not on the flat sample which is particularly intriguing despite the low index contrast by the disordered polymer. This assertion further suggests that the performance of disordered polymer is largely governed by purely structural correlation constructing the ARC rather than its material properties (details in Supplementary information, **Figure S8-S11**).

Up to this point, we have a disordered ARC that works reasonably well across the visible range up to 820 nm, so it is suitable for most emerging class of halide perovskite materials. To test the effectiveness of the disordered structures, we examined the performance of this disordered ARC on top of a triple-cation halide perovskite thin-film $[\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3]$ having absorption tail around 780 nm, and evaluated spatially and spectrally the light absorption with respect to bandgap of this archetypical perovskite. **Figure 2a** shows simulated spatial distribution of carrier generation rate of the perovskite film at different excitation frequency, near- $(0.96 \lambda/E_g)$ and half-of the bandgap $(0.5 \lambda/E_g)$, after filtered by the actual reconstructed patterns of disordered ARC. This carrier generation rate represents the number of electron-hole pair's density per unit volume under unpolarized light source at different frequency and can be associated to the strength of light absorption. The carrier generation rate is strongly localized near the bandgap, but becomes more homogeneously distributed at half of the bandgap frequency. This is particularly beneficial, because most perovskite materials absorb relatively weakly near the bandgap, but strongly at half-of the bandgap. Nevertheless, in both cases, the disordered speckle patterns are clearly visible. It is exhilarating that the speckle patterns not only occur on the surface, but also transferable to the underlying perovskite thickness, and as a result modifying carrier generation rate profile of the film beyond the standard decay of Beer-Lambert model (see the panels of cross-section in **Figure 2a**). This highlights the benefit of doing light management in low-index materials such as polymer ARC; not only providing optical index match between free-space (air) and perovskite, but also modifying the spatial distribution of electromagnetic modes readily

transferable to the underlying film. The spatial correlation of the speckle patterns justifies the strength of this photon diffusion toward the perovskite film.

To give insight on how the spatial arrangement of speckle patterns affects perovskite absorption, we evaluate a periodic pattern against the disorder pattern ARC. **Figure 2b** shows that the disordered pattern is superior compared to the periodic, and reference (without ARC). Note that, the periodic pattern may surpass the disordered one if its periodicity is carefully tuned, but for the sake of commensurate study, the periodicity here is set to the average spatial distance of the disorder pattern.²³ The simulation shows that the disordered ARC enables absorption enhancement of the perovskite thin film by a factor of 1.6 compared to 1.2 enhancement using periodic ARC. The superior absorption of perovskite using disordered ARC is further retained at higher incident angle which is important for actual solar cell application in terrestrial condition (**Figure S12**). Interestingly, using disordered polymer ARC, there is no speckle randomness appearing in the absorption spectrum of perovskite, this is in contrast to typical spectrum of disordered patterns directly applied on high-index contrast materials (e.g. silicon-air interfaces);⁸ again highlighting the benefit of light-management in low-index polymer medium that does not drastically modify the absorption spectrum of the underlying film, but rather enhance its broadband absorption intensity.

Next, to understand how specifically the disordered arrays contributes to enhance the perovskite absorption, we decomposed the two-dimensional SEM image of the actual disordered PDMS micro-pyramids (**Figure S1**) into binary images consisting of three-arrays of scattering centers, here called junction point array, boundary network, and peak point array (**Figure 2c**). The junction is a point array connecting the neighboring pyramidal bases, the boundary is a line array constructing the pyramidal bases, and the peak is a point array of pyramidal summits. Since the complex index of the polymer is low and presumably constant, then we can directly transform these real space arrays to reciprocal space to identify the characteristic contribution of each scattering center at different frequency and angle. The junction, boundary, and peak arrays show very distinct features in reciprocal space which indicates that the disordered polymer ARC is not random, but structurally correlated. At higher frequency approaching the region around the origin of reciprocal space, the feature becomes highly circular and continuous (isotropic symmetry), but becomes more discretized resembling whispering gallery modes at lower frequency, except for the boundary array (see the Fourier images in **Figure 2d**). When averaged over statistically large

sample, these reciprocal spaces can carry important information of all optical modes that is the solution of photon diffusion toward the underlying perovskite thin-film. We then applied this information on top of the perovskite surface, to simulate its total absorption. **Figure 2d** shows that the peak point array is the dominator contributing to the perovskite absorption, especially at near-bandgap ($0.96 \lambda/E_g$). The absorption using the peak point array however drops around the half-bandgap ($0.5 \lambda/E_g$), this is probably due to the more discontinuous rings in the reciprocal space that leads to prohibiting light transmission at every periodic angle which otherwise is in favor of the perovskite absorption. So, we expect that the presence of junction and boundary arrays of the micro-pyramids compensates such loss, hence explaining the broadband absorption enhancement in **Figure 2b**.

Finally, we experimentally integrated this disordered polymer ARC onto a borosilicate glass superstrate of a fully integrated triple-cation perovskite solar cell (**Figure 3a**)²⁴ and demonstrated power-conversion-efficiency improvement from 17.12 % to 17.54 % without modifying the open-circuit voltage and fill-factor of the original device (**Table 1**). A hysteresis behavior of the transient current-voltage characteristic of the device often makes accurate efficiency comparison challenging, but overall, we always obtained a higher short-circuit current density, thus efficiency of the device, with the disordered polymer ARC. A reduced efficiency may happen only in the case when the structural arrangement of the ARC is completely random, so there is lack of structural correlation. To support the effectiveness of disordered ARC, we carried out a full-device simulation (coupled optical-electrical modelling) at steady-state condition by taking into account all optical index and realistic electrical parameters in every layer as simulation inputs.²⁵ The simulation suggests that our perovskite device can be improved further to 19.59 % efficiency using identical characteristics of disordered polymer ARC as demonstrated here (**Figure 3b**, details in supporting information). The charge collection efficiency enhancement occurs over 350 to 780 nm wavelengths (see EQE in **Figure 3c**), and the absorption remains efficient even at high angles of irradiation (**Figure S11**). The discrepancy between the experiment's and simulation's efficiency values is due to the fact that the ARC area covering the experimental cell is not fully forming disordered structures. Another limiting factor is due to imperfect replication of textured PDMS from the Si master ($\sim 3 \text{ mA/cm}^2$ loss) and surface defects (wrinkles) on the PDMS ($\sim 0.35 \text{ mA/cm}^2$ loss), so in theory, approximately 3 to 4 % absolute efficiency gain is possible on perovskite solar cells depending on bandgap. Such enhancement is similar to the gain

typically achieved by direct micro-pyramid texturing of Si cell compared against a flat Si cell.^{7,11} For halide perovskite thin-films, this number is highly encouraging, because we do not need to modify the device architecture, but only require optically textured ARC which opens avenues for further light-management. This statement is only valid as long as there is a sufficient structural correlation (disorder) within the ARC as shown in this work.

To summarize, the disordered polymer anti-reflective coating may provide a powerful photon-management platform for improving the light-harvesting of photovoltaics without modifying the original device architectures. Combining experiments and simulation, we realized the flexibility to engineer the shape, arrangement, dimensionality, and structural correlation of the disordered patterns within the micro-pyramid PDMS textures for an efficient anti-reflective coating (ARC). Within the ARC, we demonstrate a total reflectance down to 5% while retaining high optical transmission of 94 % across 300 to 820 nm wavelength before the photonic bandgap effect from the disorder starts to dominate. This working frequency is particularly useful for a wide-range of perovskite solar cells. We integrated this design in $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ halide perovskites and obtained 1.6-fold absorption enhancement leading to 17.54 % and 19.59 % of experimental and simulated power-conversion efficiency, respectively. A prevalent brute force approach for disordered patterning, however, is not necessarily useful as ARC. This explains why some textures work, but others do not. Instead, understanding structural arrangement of junction, boundary, and peak scattering arrays of the micro-pyramid PDMS is probably the key to enhance energy delivery from free space (air) to perovskite solar cells which is particularly useful at diffuse sunlight. Considering all possible fabrication defects, we predicted that around 3 to 4 % absolute power-conversion-efficiency gain of perovskite solar cells is practically reasonable to achieve using disordered polymer micro-pyramid ARC, without having to modify the device architectures. The disordered pattern is not limited to micro-pyramids, but optimizing the structural correlation of the disorder using low-index anti-reflective coatings will be an exciting direction for future research, for instance to specifically target near-bandgap absorption improvement for this emerging class of solar cell materials by photon localization,¹⁴ directional light emission,^{12,13} disorder hyperuniformity,^{15,16} and even thermal emission management.²⁶

Supporting information

Details in Sample preparation, Optical characterization, Device fabrication and characterization, Optical simulation, Device simulation

Acknowledgments

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Figures

Figure 1. Disordered micro-pyramid anti-reflective coating (ARC) made by PDMS polymer. (a) Schematic. (b) Photograph of digital “9” red-LED covered with the disordered ARC, (c) Photograph of “white” appearance of the disordered ARC at long focal-distance to the object. Experimentally measured reflectance (d) and transmission (e) spectra of the disordered ARC. This disordered polymer ARC has a transmission cut-off of photonic bandgap at 820 nm, so beneficial for various types of halide perovskite solar cells (more details in Supporting information).

Figure 2. (a) simulated spatial carrier generation rate of the perovskite at different excitation wavelength (near the bandgap $0.96 \lambda/E_g$, and half of the bandgap $0.5 \lambda/E_g$ of $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ halide-perovskite). (b) simulated absorption spectrum of the perovskite film with (periodic vs. disordered array) and without (reference) ARC. (c) binary image showing junction, boundary, and peak constructing the disordered ARC. (d) simulated absorption of perovskite film after two-dimensional Fourier decomposition of scattering contribution from junction, boundary, and peak scattering arrays (also shown by their images in reciprocal space).

Figure 3. Perovskite solar cells performance using disordered anti-reflective coating (ARC). **(a)** Schematic of the device architecture, **(b)** simulated current-voltage (I - V) curve under AM 1.5 standard illumination, and **(c)** simulated external quantum efficiency (EQE) of the perovskite cell with (disordered vs. periodic) and without (reference) ARC. The experimental and simulated device performance characteristics are listed in **Table 1**.

Table 1. PV characteristics

PV parameter ¹	reference (no ARC)		periodic	disorder	
	measured	simulated	simulated	measured	simulated
V_{oc} (Volt)	1.159	1.159	1.162	1.161	1.161
J_{sc} (mA/cm ²)	19.98	21.17	22.46	20.31	23.02
FF	0.73	0.72	0.71	0.74	0.72
PCE (%)	17.12	17.99	19.09	17.54	19.59

ToC

Disordered-, rather than random-, micro pyramid polymer anti-reflective coating (ARC) demonstrates a strong photonic effect leading to a total reflectance of 5 % and transmission of 94 % across 300 to 820 nm wavelength. Disordered point and line arrays constructing the ARC are the key to deliver 1.6-fold absorption gain leading to 19.59 % efficiency of perovskite solar cells.