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Optical absorption enhancement in NH₂CH=NH₂Pbl₃ lead halide perovskite solar cells with nanotextures

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Abstract

This article reports, for the first time to our knowledge, that the power conversion efficiencies (PCEs) of planar NH₂CH=NH₂PbI₃ (FAPbI₃) lead halide perovskite solar cells (SCs) can be largely improved by fabricating nanotextures on the SC surface. Four kinds of nanotextures are investigated and compared with each other: column hollow (CLH) nanoarrays, cone hollow (CNH) nanoarrays, square prism hollow (SPH) nanoarrays, and pyramid hollow (PYH) nanoarrays. Compared with the PCEs of the planar SCs with the same layer depth *d*, it is found that when *d* is in the range of 125–500 nm and when the array period, as well as the filling fraction of the nanotexture, are optimized, the ultimate efficiency increased 29%–50% for the CLH and SPH textured FAPbI₃ SCs relative to the planar ones. When *d* < 250 nm, the optimized ultimate efficiencies of the CLH and SPH textured FAPbI₃ SCs with optimized nanotextures are higher than those of the CNH and PYH ones, and vice versa. The reasons why fabricating nanotextures on SC surfaces can largely improve the PCE of the FAPbI₃ SCs are discussed.

Keywords: nanotexture, perovskite solar cell, ultimate efficiency, FDTD method, optical absorption

(Some figures may appear in colour only in the online journal)

1. Introduction

Nowadays, solar cell (SC) research has been driven by the need of fabricating SCs with high power conversion efficiency (PCE), yet low cost and long-term stability. In recent years, the skyrocketing PCE of metal halide perovskite SCs has stunned the photovoltaic community. The newly emerged organic–inorganic trihalide perovskite light-absorption materials all have the molecular formulation of ABX₃, where A⁺ is usually methylammonium (CH₃NH₃⁺, or MA⁺) or formamidinium (NH₂CH=NH₂⁺, or FA⁺) cation, B²⁺ is

commonly lead cation (Pb²⁺), and X^- is halide anion (Cl⁻, Br⁻, or I⁻).

Much perovskite SC research has been based on the CH₃NH₃PbI₃ (MAPbI₃) or CH₃NH₃PbI_{3-x}Cl_x (MAPbI_{3-x}Cl_x) perovskite materials. The energy band gaps, E_g , of the MAPbI₃ and MAPbI_{3-x}Cl_x materials are ca. 1.5–1.6 eV [1–4], and ca. 1.6–1.9 eV [5–7], respectively, which are obviously larger than the ideal E_g for photovoltaic light absorption materials of 1.1–1.4 eV, which is derived from the Shockley–Queisser limit [8]. Lately, the novel NH₂CH=NH₂PbI₃ (FAPbI₃) perovskite material has drawn tremendous attention. For example, in [9], a highest PCE of 20.1% in a FTO/TiO₂/FAPbI₃/PTAA/Au structured perovskite SC has been reported, in which the

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perovskite FAPbI₃ layer adopts the planar structure. In their study, the planar FAPbI₃ layer is fabricated by an intramolecular exchange process so that the as-annealed layer can be dense and uniform. In our very recent research, the refractive index and extinction coefficient $n(\lambda)$ and $k(\lambda)$ as functions of λ , as well as the bandgap E_{g} of the FAPbI₃ material, are measured with the spectroscopic ellipsometry (SE) method [10]. It is found that, compared with MAPbI3, the FAPbI3 material has smaller bandgap $E_g = 1.45 \text{ eV}$, which allows absorption in broader wavelength; smaller $n(\lambda)$, which brings smaller surface reflection when solar light is vertically incident on the SC surface; and much larger $k(\lambda)$ when λ is 400–700 nm, which leads to stronger photon absorption when the material is applied as the SC photovoltaic material. With so many advantages, the FAPbI₃ material has great potential in future perovskite SC manufacturing, and the SCs made of it are believed to be able to make breakthroughs over 25% in PCE [1, 9, 11]. However, although almost two to three years have passed and various methods have been proposed, the highest PCE remains $\sim 22\%$. New approaches have been made to partially replace the FA⁺ cation with the MA^+ or Cs^+ cation. A stable PCE as high as 21.1% has been achieved with the planar-structured SC structure of FTO/compact TiO2/Li-doped mesoporous TiO2/Cs0.05 $(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3/spiro-OMeTAD/Au.$ From the perspective of physics, one major disadvantage of the $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ material and the like is that they have higher E_g and no obvious better light-absorption properties, which sets a ceiling for their potential.

Apart from optimizing the SC photovoltaic material, one important method to enhance the PCE is to improve the SC structure, especially the light-absorption layer. It has been clarified that fabricating nanotextures on SC surfaces can largely improve optical absorption due to the light-trapping effect, so that the PCE can be much increased. It has been pointed out that usually, if the period of the nano texture is comparable to or smaller than the wavelength of incident photons, enhanced solar light-trapping can occur through multiple scattering and wave interference [12, 13]. Light in certain dielectric microstructures exhibits localized modes, similar to the localized wavefunctions of electrons in disordered solids, and the light-absorption enhancement by these localized modes contributes to the improvement of the PCE [12, 14–16]. In manufacturing, the nanotextures are varied in their geometrical structures. For example, column-shaped pillar (CLP) nanoarrays [17-22], column-shaped hollow (CLH) nanoarrays [22-24], cone-shaped pillar (CNP) nanoarrays [24-27], cone-shaped hollow (CNH) nanoarrays [28], square prism hollow (SPH) nanoarrays [29–31], and pyramid hollow (PYH) nanoarrays [32]. In our previous research it was found that, when the SC light absorption layer depth, d, is set from 31.25 to 2000 nm, compared with those of the planar SCs, the optimized ultimate efficiency of the nanotextured SCs increased from 86% to 322% relative to the planar ones for the c-Si SCs [33] and from 65% to 179% relative to the planar ones for the a-Si:H(10%H) SCs [34]. This phenomenon has been confirmed by experimental facts in the silicon SCs. For example, in Savin et al's research, it has been demonstrated that the PCE of black silicon solar



Figure 1. Geometric structures of the four kinds of FAPbI₃ nanotexture arrays. The solid part is the FAPbI₃ material, and the material filled within the nanotextures is air. (a) CLH arrays, (b) CNH arrays, (c) SPH arrays, (d) PYH arrays, (e)–(h) one period of nanotexture array with three different f in the two-dimensional square lattice. (e) CLH units, (f) CNH units, (g) SPH units, (h) PYH units.

cells can reach 22.1% by providing excellent chemical and electrical passivation [35]. It is very interesting to study how much the PCEs of the perovskite FAPbI₃ SCs can be improved when nanotexture is introduced to their surfaces.

In this article, four kinds of important nanotextures are investigated: the CLH, CNH, SPH, and PYH arrays (see figure 1). The geometrical parameters of these four kinds of nanotextures include the SC's photovoltaic absorption layer depth *d*, the filling factor *f*, and the periodical length of the two-dimensional periodical square lattice *p*. In our study, *f* is defined as the ratio of the volume of the FAPbI₃ material to that of the planar film. For a fixed type of nanotexture and *d*, the ultimate efficiency, i.e. the ideal efficiency without considering carrier recombination, is optimized over *f* and *p*, and is defined as the optimized ultimate efficiency, η_0 . Using the finite difference time domain (FDTD) method, it is demonstrated that when optimized nanotexture is fabricated on the



Figure 2. Basic structure of the analyzed solar cells in the FDTD simulation region.

SC surface, the PCE of the perovskite FAPbI₃ SC can be largely improved. For the FAPbI₃ layer, when the layer depth is in the range of 125–500nm and when the nano texture is optimized, in comparison with the planar SCs, PCEs increased 29%–50% for the CLH and the SPH textured FAPbI₃ SCs relative to the planar ones, and 20%–41% for the CNH and PYH textured FAPbI₃ SCs relative to the planar ones.

2. Methods

The FDTD simulations are performed with the Lumerical FDTD Solutions program (Edition 8.6). The FDTD simulation region is shown in figure 2. In the FDTD simulations, when solar light is vertically incident upon the FAPbI₃ SC's upper surface along the *x*-axis, the FDTD method is applied to acquire the reflectance (*R*) and transmittance (*T*) of the SC by FDTD power monitors #1 and #2 [33, 34, 36]. The absorptance (*A*) is then determined by $A(\lambda) = 1 - R(\lambda) - T(\lambda)$. The range of wavelength in the calculation, λ , is set from 300 to 900 nm, with a step of $\Delta \lambda = 1$ nm, in which the solar irradiation is strong. Moreover, this range covers the light-absorption range of the FAPbI₃ material, whose bandgap wavelength, $\lambda_g = 855$ nm [10].

The FAPbI₃ SCs are set as two-dimensional square lattice nanotextures. The bottom planes of the FaPbI₃ SCs are set to be parallel to the y-z plane. A y-polarized plane wave broadband source is incident upon the FAPbI₃ SC from the top, along the x-axis. Symmetric and antisymmetric boundary conditions were adopted in the y and z directions, respectively [33]. The perfectly matched layer (PML) boundary conditions

Z Xie et al

are employed in the *x* direction. The space outside the SC is filled with air (n = 1, k = 0). From both front and back sides of the SC to the PML boundary conditions, a distance of $d_{\text{air}} = 1000 \text{ nm}$ is set, and the thickness of PML is set to be $d_{\text{PML}} = 360 \text{ nm}$ [33, 34].

Until recently, the majority of the perovskite SCs took a perovskite light-absorption material layer depth, d, at ca. 100 nm ~ 500 nm. In our FDTD simulation, this range is extended to from $1/32 \ \mu m$ to $2 \ \mu m$ in an exponential sequence, i.e. 31.25, 62.5, 125, 250, 500, 1000, and 2000 nm.

For the CLH texture, when the outer rim of the air-filled column is tangent to the square lattice, f achieves the minimum of $1 - \pi/4$. Therefore, in simulation, f is set as 1 - 0.2, 1 - 0.3, ..., 1 - 0.7, and $1 - \pi/4$. For the CNH texture, when the outer rim of the air-filled column is tangent to the square lattice, f achieves the minimum of $1 - \pi/12$. Therefore, in simulation, f is set as 1 - 0.5/3, 1 - 0.6/3, 1 - 0.7/3 and $1 - \pi/4/3$. For the SPH texture, f is set as 1 - 0.1, 1 - 0.2, ..., 1 - 0.7, and 1 - 0.8. For the PYH texture, when the outer rim of the bottom of the square pyramid is the same as the square lattice, f achieves the minimum of 1 - 1/3. Therefore, in simulation, f is set as 1 - 0.5/3, 1 - 0.6/3, ..., 1 - 0.9/3, and 1 - 1/3. For the CLH and the SPH textures, p is set from 0.3 to $0.8 \,\mu$ m, $0.1 \,\mu$ m stepped. For the CNH and PYH textures, p is set from 0.3 to $1.1 \,\mu$ m, $0.1 \,\mu$ m stepped.

In 1961, to calculate the upper theoretical limit for the efficiency of a *p*–*n* junction SC, Shockley *et al* proposed the theory of detailed balance limit of efficiency [37]. Based on Shockley's theory, in 2010, Han and Chen defined the ultimate efficiency without considering carrier recombination, η_{un} , to evaluate the solar light-absorption performance of SCs. In their method, η_{un} is defined as the efficiency of a photovoltaic cell as the temperature approaches 0 K, when each photon with energy greater than the band gap produces only one electron–hole pair [23]:

$$\eta_{\rm un} = \frac{\int_0^{\lambda g} I(\lambda) A(\lambda) \frac{\lambda}{\lambda g} d\lambda}{\int_0^\infty I(\lambda) d\lambda}.$$
 (1)

In equation (1), $I(\lambda)$ stands for the solar irradiance and is depicted in the standard AM 1.5 Direct + Circumsolar spectrum [38], $A(\lambda)$ is the absorptance, λ is the wavelength, and $\lambda_g = 855$ nm [10] is the wavelength corresponding to the band gap of the FAPbI₃ material. In this equation, for a given absorption and solar radiation spectrum, λ/λ_g can be regarded as a weighting factor for integration. As the wavelength decreases from the band gap wavelength, the contribution of the absorbed solar energy to the ultimate efficiency decreases because the excess energy of photons above the band gap is wasted.

The major advantage of equation (1) is that it is purely derived from the fundamental physics of the photovoltaic process, and the calculation only requires the material's basic optical index and E_g . Moreover, the relatively complex experimental parameters and/or empirical formula that may possibly bring uncertainties, even errors, to the calculated ultimate efficiency have been avoided. Thus, equation (1) has been widely cited to calculate the upper theoretical limit for the efficiency of SC [28, 33, 34, 39, 40].

On the other hand, in perovskite SC manufacturing, as the perovskite light-absorption material is basically an organic-inorganic hybrid compound, carrier recombination greatly affects the improvement of PCEs for the SCs [6, 7]. However, via enhancements by optimizing fabrication techniques, the disadvantages caused by carrier recombination can be reduced to the least extent [1, 5, 7]. For the FAPbI₃ material, very recently, in [41], the researchers proposed a new process combining the cooling solution and inverse temperature crystallization methods to fabricate a single-crystal α phase FAPbI₃ material. The diffusion length of their acquired single-crystal α -phase FAPbI₃ material achieved 2.2 μ m, which is larger than our calculated d upper limit of 2 μ m. The perovskite materials have shown potential in their enhancement space in diffusion length. For example, for the MAPbI₃ material, with the method proposed by Dong et al, the diffusion length achieved 175 µm [2]. Very recently, in Li et al's research, with a similar single crystal-fabrication method in [41], the diffusion length for FAPbI₃ achieved 118 μ m [42]. In future SC development, it is predictable that the diffusion length for the α -phase FAPbI₃ in the perovskite SCs can be further extended to even larger scales.

For the FAPbI₃ material, to the best of our knowledge, its surface recombination velocity S_n has not been clarified. Usually for thin films, the surface recombination at grain boundaries determines the effective carrier lifetime [43], so to minimize the effect of surface recombination, the grain size should be large enough. This defect can be overcome by fabricating a single crystal as the light-absorption layer, as proposed by [41]. Another source of surface recombination is the up and down interfaces of the perovskite light-absorption layer in the SCs. In MAPbI₃ SCs, it has been clarified by [44–46] that by depositing materials such as C₆₀ or PCBM [39, 47] the dangling bonds of the MAPbI₃–TiO₂ interface can be largely reduced, which is directly reflected in the reduction of hysteresis in the sequential/reversed J–V curve of the SC [44–46].

With these considerations, the effect of carrier recombination does not affect the calculation of the SC ultimate efficiency, η_{un} , for the SCs.

3. FDTD simulation results

The calculated η_{un} of the CLH, CNH, SPH, and PYH nanotextured FAPbI₃ SCs at different layer depth *d*, filling factor *f*, and period *p* are presented in figures 3(a)–(d). In order to compare the calculated η_{un} with the planar, non-textured FAPbI₃ SCs, the η_{un} of the planar SCs, η_p , at different *d*, are also shown.

As can be seen in figures 3(a)–(d), the η_{un} of these four kinds of nanotextured FAPbI₃ SCs are the functions of *d*, *f*, and *p*. For a decided nanotexture type and *d*, the optimized ultimate efficiency, η_0 , is defined as the ultimate efficiency η_{un} optimized over *f* and *p* [33, 34]. The simulation results have shown that for a decided nano texture type, d and f, usually the period around 400–600 nm optimizes η_{un} . This phenomenon is consistent with what we have observed in c-Si [33] and a-Si:H [34] photovoltaic materials. It is generally explained that, in the light trapping effect, when the period of the two-dimensional nanotexture, p, is near the incident photon wavelength, λ , a quite high absorptance can be acquired with the texture so that quite high η_{un} can be achieved [34]. The peak of the AM 1.5 Direct + Circumsolar spectrum is located at around 500–600 nm, and therefore η_{un} is optimized when p is in this range, regardless of the nanotexture type, d or f.

In the CLH textured FAPbI3 SCs, as presented in figure 3(a), when d increased from 31.25 to 2000 nm, the f that optimizes η_{un} to η_0 decreased from 1 - 0.3 to $1 - \pi/4$, which is the minimum of f for the CLH texture. Similarly, in the SPH textured FAPbI₃ SCs as presented in figure 3(c), when d increased from 31.25 to 2000 nm, the f that optimizes $\eta_{\rm un}$ to η_0 decreased from 1 - 0.2 to 1 - 0.7. This phenomenon exists in the CNH and PYH textured FAPbI3 SCs when d is large. In the CNH textured FAPbI₃ SCs, as presented in figure 3(b), when d increased from 125 to 2000 nm, the f that optimizes η_{un} to η_0 decreased from 1 - 0.6/3 to $1 - \pi/4/3$, which is the minimum of f for the CNH texture. In the PYH textured FAPbI₃ SCs, as presented in figure 3(d), when d increased from 125 to 2000 nm, the f that optimizes η_{un} to η_0 decreased from 1 - 0.6/3 to 1 - 1/3, which is the minimum of f for the PYH texture.

4. Discussions

Letting $A(\lambda) = 1$ in equation (1), the limiting value of η_0 for the FAPbI₃ material can be calculated as 43.8%. In figure 4, the $\eta_0(d)$ for FAPbI₃ SCs with the CLH, CNH, SPH, and PYH nanotextures are compared with those for the planar, non-textured FAPbI₃ SCs with the same *d*, which is defined as $\eta_p(d)$. The increment percentage of ultimate efficiency, δ (*d*), is correspondingly defined as the following: $\delta(d) =$ $(\eta_0(d)/\eta_p(d) - 1) \times 100\%$.

In figure 4, the Yablonovitch limit for the ultimate efficiency is also presented [48, 49]. Usually, assuming perfect antireflection and light trapping, the absorption spectrum in a thin photovoltaic film with thickness *d* is given by the Yablonovitch limit: $A_{\text{Yablonovitch}}(\lambda) = 1 - 1/(1 + 4(n(\lambda))^2 \cdot \alpha(\lambda) \cdot d)$, in which $\alpha(\lambda) = (4\pi k(\lambda))/\lambda$ is the absorption coefficient [50]. The $A_{\text{Yablonovitch}}(\lambda)$ for the FAPbI₃ material is substituted into equation (1) and the corresponding Yablonovitch limit for the ultimate efficiency of the FAPbI₃ material is acquired. In previous studies, it has been pointed out that the Yablonovitch limit is applicable only when *d* is large enough, i.e. when $d > \lambda/(2n(\lambda))$ [51]. Therefore, in figure 4, the d > 125 nm curve of the Yablonovitch limit for the ultimate efficiency is presented.

Several conclusions can be acquired from figure 4. Firstly, with the same FAPbI₃ SC depth, *d*, when d > 125 nm, the η_0 of these four kinds of nanotextured FAPbI₃ SCs is much larger than that of the planar, non-textured



Figure 3. η_{un} for nanotextured FAPbI₃ SCs with different layer depth *d*, filling factor *f*, and period *p*. For each *d*, the corresponding optimized η_{un} , η_0 , is marked with a black arrow beneath. η_p is the η_{un} of the planar, non-textured FAPbI₃ SCs. (a) CLH, (b) CNH, (c) SPH, (d) PYH.

ones. For example, when d = 125 nm, $\eta_0 = 29.8\%$ for the CLH textured FAPbI₃ SCs, while the corresponding $\eta_p = 20.8\%$ and $\delta = 43.1\%$. When d = 250 nm, $\eta_0 = 33.4\%$ for the CLH textured FAPbI₃ SCs, while the corresponding $\eta_p = 24.3\%$ and $\delta = 37.3\%$. When d = 500 nm, $\eta_0 = 39.7\%$ for the PYH textured FAPbI₃ SCs, while the corresponding $\eta_p = 28.2\%$ and $\delta = 40.7\%$. The increase of light absorption in the optimized nanotextured FAPbI₃ SCs compared with that of the planar, non-textured ones is manifested.

Secondly, as *d* increases beyond 125 nm, the highest η_0 value of the four kinds of nanotextures approaches the corresponding Yablonovitch limit for the ultimate efficiency. For example, when d = 125 nm, $\eta_0 = 29.8\%$ for the CLH textured FAPbI₃ SCs, which is 87.3% of the Yablonovitch limit. When d = 250 nm, $\eta_0 = 33.4\%$ for the CLH textured FAPbI₃ SCs, which is 88.3% of the Yablonovitch limit. When d = 500 nm, $\eta_0 = 39.7\%$ for the PYH textured FAPbI₃ SCs, which is 98.4% of the Yablonovitch limit. When d = 2000 nm, $\eta_0 = 42.5\%$ for the CNH textured FAPbI₃ SCs, which is already 99.1% of the Yablonovitch limit.

Thirdly, the $\eta_0(d)$ values for the CLH textured FAPbI₃ SCs are very close to those for the SPH textured ones. When d > 62.5 nm, the $\eta_0(d)$ values for the CLH textured FAPbI₃ SCs are larger than those for the SPH textured ones and

vice versa. With the same *d*, the largest difference of only 0.9% in absolute $\eta_0(d)$ value happens at d = 250 nm. Similarly, the $\eta_0(d)$ values for the CNH textured FAPbI₃ SCs are very close to those for the PYH textured ones. The $\eta_0(d)$ values for the CNH textured FAPbI₃ SCs are larger than those for the PYH textured ones in most *d* cases studied, except the d = 300 and 500 nm cases. With the same *d*, the largest difference of only 0.3% in absolute $\eta_0(d)$ value happens at d = 200 nm.

Lastly, for the FAPbI₃ material, a critical turning depth $d_c \approx 250 \text{ nm}$ exists. When $d < d_c$, the η_0 values of the CLH and SPH textured FAPbI₃ SCs are larger than those of the CNH and PYH textured ones and vice versa. This phenomenon is similar to what our group has previously reported in c-Si [33] and a-Si:H(10%H) [34] materials.

In a word, with the FDTD simulations, it is demonstrated that the introduction of nanotextures on the FAPbI₃ SC surface would greatly increase the ultimate efficiency. To find the fundamental reasons for this phenomenon, the absorption, reflection, and transmission spectrum for the planar, nontextured FAPbI₃ SCs are investigated and they are compared with those for the SCs with optimized nanotextures.

The $A(\lambda)$, $R(\lambda)$, and $T(\lambda)$ for the planar, non-textured FAPbI₃ SCs at different *d* are presented in figures 5(a)–(c).



Figure 4. (a) Comparisons between η_0 for the CLH, CNH, SPH, and PYH textured FAPbI₃ SCs with those of the planar ones, when *d* ranges from 1/128 to 2 μ m. (b) Comparisons between δ for the CLH, CNH, SPH, and PYH textured FAPbI₃ SCs, and the corresponding Yablonovitch limit.

From figure 5(a), it can be seen that when *d* increases from 31.25 to 2000 nm, in all λ ranges studied, $A(\lambda)$ monotonously increased. However, when *d* increases from 125 to 2000 nm, in the $\lambda < 500$ nm wavelength range, $A(\lambda)$ increases little. The major reason why η_p only increases from 20.8% to 32.9% when *d* increases from 125 to 2000 nm is that the absorption rate near the band gap is greatly improved. The origin of this improvement is found in figures 5(b) and (c).

In figure 5(b), when *d* increases from 31.25 to 2000 nm, in all λ ranges studied, the reduction of the corresponding $R(\lambda)$ is not obvious, especially in the λ range of ca. 500–700 nm, where the AM 1.5 Direct + Circumsolar irradiation is large. However, in figure 5(c), when *d* increases from 125 to 2000 nm, the reduction of $T(\lambda)$ is very obvious. Considering that $A(\lambda) = 1 - R(\lambda) - T(\lambda)$, from figures 5(a)–(c) it can be concluded that in the planar, non-textured FAPbI₃ SCs, when *d* increases from 125 to 2000 nm, the increases from $T(\lambda)$, which decreases greatly, rather than $R(\lambda)$. To fabricate FAPbI₃ SCs with PCE as high as possible, it is critical to reduce $R(\lambda)$.

The comparisons of $A(\lambda)$, $R(\lambda)$, and $T(\lambda)$ between the planar FAPbI₃ SCs and those of the FAPbI₃ SCs with the optimized nanotextures when *d* is from 31.25 to 2000 nm are presented in figures 6(a)–(g). In all *d* studied, in the λ range of 500–700 nm, where the peak of the AM 1.5 Direct + Circumsolar irradiation is large, the $A(\lambda)$ values of the optimized nanotextured FAPbI₃ SCs are much larger than those of the



Figure 5. Absorptance $A(\lambda)$, reflectance $R(\lambda)$, and transmittance $T(\lambda)$ when d = 31.25, 62.5, 125, 250, 500, 1000, and 2000 nm. (a) $A(\lambda)$, (b) $R(\lambda)$, and (c) $T(\lambda)$.

planar ones. When d > 250 nm, in all λ range studied, the A (λ) values of the optimized nanotextured FAPbI₃ SCs are larger than those of the planar ones with the same d. The reason why optimized nanotextured FAPbI₃ SCs have larger $A(\lambda)$ values than the planar ones with the same d lies in the fact that they have much smaller reflection rate, $R(\lambda)$, especially in the λ range of 500–700 nm. When d < 500 nm, the T (λ) values of the FAPbI₃ SCs with optimized nanotextures are larger than those of the planar ones by ca. 0.1–0.2 in the in the λ range of ca. 300–550 nm. This phenomenon does not affect the ultimate efficiency advantage of the FAPbI₃ SCs with optimized nanotextures much, because the solar irradiation in this λ range is relatively small. When d is larger than 500 nm, generally, both $R(\lambda)$ and $T(\lambda)$ values of the FAPbI₃ SCs with optimized nanotextures are smaller than those of the planar ones with the same d. The major reason that the η_0 values of the FAPbI₃ SCs with optimized nanotextures are larger than



Figure 6. Comparisons of $A(\lambda)$, $R(\lambda)$, and $T(\lambda)$ between the planar FAPbI₃ SCs and the FAPbI₃ SCs with optimized nanotextures at (a) d = 31.25 nm, (b) d = 62.5 nm, (c) d = 125 nm, (d) d = 250 nm, (e) d = 500 nm, (f) d = 1000 nm, and (g) d = 2000 nm.

the η_p values of the planar, non-textured ones is that they have much smaller $R(\lambda)$, especially in the λ range of ca. 500–700 nm.

The perovskite materials, including e.g. MAPbI₃, MAPbI_{3-x}Cl_x, as well as FAPbI₃, are fundamentally metal– organic compound materials, and they are relatively soft compared with the conventional inorganic photovoltaic materials such as c-Si, a-Si:H, CdTe, and GaAs. Many methods can be used to fabricate nanotextures on the metal– organic FAPbI₃ film, and one of the potential methods is the nanoimprint lithography technique [52–54]. With the optimized nanotextures, it can be expected that FAPbI₃ SCs with PCEs as high as 25% or even higher can be acquired.

Another potential advantage of nanotextured FAPbI₃ SCs is that the light-absorption properties of the nanotextures may help to prevent the FAPbI₃ material inside the FAPbI₃ SCs from decomposing as the result of absorbing too many highenergy photons. As can be seen from figure 5, generally the planar, non-textured FAPbI₃ SCs have the largest $A(\lambda)$ in the wavelength range of ca. 300-400 nm due to the fact that FAPbI₃ material's $k(\lambda)$ is the largest in this wavelength range. However, the $A(\lambda)$ of the FAPbI₃ SCs with optimized nanotextures is the largest in the wavelength range of ca. 500-700 nm due to the light-trapping effect, as can be seen form figure 6. The bandgap of the FAPbI₃ material measured by the SE spectroscopic ellipsometry method is $E_g =$ 1.45 eV, and the corresponding wavelength $\lambda_g = 855$ nm. Photons with energy E, which is larger than E_g , are absorbed by the FAPbI3 material. In this process, the residual energy of $E-E_g$ is absorbed by the lattice in the form of heat. The photons with wavelength near the ultraviolet light wavelength range leave much more residual heat than the photons with wavelength in the range of ca. 500-700 nm. This residual heat has little effect on the conventional inorganic photovoltaic materials, because they are relatively stable. However, for the FAPbI₃ material, the accumulation of residual heat could be fatal because the FAPbI₃ material is sensitive to heat and could decompose quickly. Fabricating nanotextures on the surface of FAPbI₃ SCs has the potential to improve their stability in long-term use.

5. Conclusion

The PCEs of the planar FAPbI₃ SCs can be largely improved by fabricating optimized nanotextures on the SC surface. With the FDTD method, the ultimate efficiencies, η_{un} , of the CLH, CNH, SPH, and PYH nanotextured FAPbI₃ SCs are studied. The parameters that describe the geometrical structure of the nanotextures include: the SC layer depth *d*, the filling factor *f*, and the period of the two-dimensional square lattice *p*. For a decided nanotexture type and *d*, the optimized ultimate efficiency, η_0 , is compared with that of the planar, non-textured SC, η_p . It is found that when d > 125 nm, the η_0 values of the SCs with either kind of nanotexture is much larger than those of the non-textured ones. When *d* is in the range of 125–500 nm, compared with η_p of the same SC depth, when *f* and *p* are optimized, the ultimate efficiencies of the nanotextured FAPbI₃ SCs increased 29%–50% for the CLH and SPH textured FAPbI₃ SCs relative to the planar ones, and 20%–41% for the CNH and PYH textured FAPbI₃ SCs relative to the planar ones. Through the investigations into $A(\lambda)$, $R(\lambda)$, and $T(\lambda)$ for the planar FAPbI₃ SCs with different *d*, it is found that when *d* increases from 125 to 2000 nm, the increase of η_p mainly originates from $T(\lambda)$ that decreases greatly, rather than $R(\lambda)$. The major reason that the η_0 values of the FAPbI₃ SCs with optimized nanotextures are larger than the η_p values of the planar, non-textured FAPbI₃ SCs with the same *d* is that the nanotextured SCs have much smaller $R(\lambda)$, especially in the λ range of ca. 500–700 nm, where the solar irradiation is large.

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