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Solar Cell Light Trapping beyond the Ray Optic Limit

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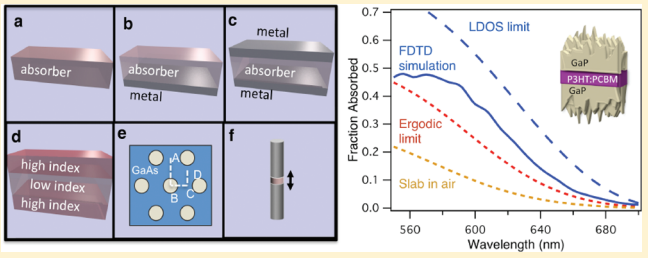
Supporting Information

ABSTRACT: In 1982, Yablonovitch proposed a thermodynamic limit on light trapping within homogeneous semiconductor slabs, which implied a minimum thickness needed to fully absorb the solar spectrum. However, this limit is valid for geometrical optics but not for a new generation of subwavelength solar absorbers such as ultrathin or inhomogeneously structured cells, wire-based cells, photonic crystal-based cells, and plasmonic cells. Here we show that the key to exceeding the conventional ray optic or so-called ergodic light trapping limit is in designing an elevated local density of optical states (LDOS) for the absorber. Moreover, for any semiconductor we show that it is always possible to exceed the ray optic light trapping limit and use these principles to design a number of new solar absorbers with the key feature of having an elevated LDOS within the absorbing region of the device, opening new avenues for solar cell design and cost reduction.



KEYWORDS: *Photovoltaic cell, solar cell, local density of optical states (LDOS), light trapping, plasmonic, nanophotonic*

To absorb nearly all of the incident sunlight, a solar cell is typically made to be optically thick and textured to improve light trapping. Using a statistical ray optics approach, the maximum light trapping absorption enhancement for a bulk absorber material with a homogeneous density of optical states is defined by thermodynamics to be $4n^2$, where n is the refractive index.[1] However, for homogeneous materials even with optimal light trapping, as the solar cell absorber layer thickness is reduced, absorption is also reduced, particularly in the wavelength range near the semiconductor bandgap, as illustrated in Figure 1a,b. For any given thickness, there is a range of wavelengths that is fully absorbed upon $4n^2$ optical passes and another range that is not fully absorbed due to the exponential nature of the absorption process and the fact that the absorption coefficient approaches zero at the semiconductor band edge (Figure 1b). Therefore, we can divide our conceptual approach to the light trapping limit between the spectral region where enhanced absorption is needed and where it is not. The transition region between these two regimes depends on the material properties, thickness, structure, etc.

There is previous evidence that solar cells with non-slablike geometries that operate in the wave optic rather than ray optic limit may exceed this limit,[3−6] and recent theoretical work has successfully explained the phenomena in selected cases.[7,8] The theory of ref 7 establishes the relationship between the modes supported in a slablike solar cell and the maximum absorption attainable but is not easily extensible to the broad portfolio of light trapping schemes currently being explored in the literature.[2,3b,9]

We find that a common defining feature of light trapping structures in the wave optical limit is that the electromagnetic local density of optical states (LDOS) integrated over the active absorber region must exceed that of the corresponding homogeneous, bulk semiconductor. That the density of optical states plays an important role in defining the light trapping limit has been alluded to in previous work,[7,10] and we use it here as a defining approach for understanding light absorption. We develop a unified framework for thin film absorption of solar radiation and show that an enhanced integrated LDOS is the fundamental criterion that determines whether light trapping structures can exceed the ray optic light trapping limit, leading to a strategy for design of solar absorber layers with wavelength-scale characteristic dimensions that exhibit optimal light trapping.

As in the original ray optics formulation,[1] the electromagnetic energy density serves as a starting point for examining the partitioning of energy between the solar cell and the surrounding environment. For any given geometry, the electromagnetic energy density is a function of position. One way to express the electromagnetic energy density is in terms of the local density of optical states (LDOS), $\rho(r,\omega)$, the modal occupation number $\langle\nu\rangle$, and the energy of each mode, $\hbar\omega$:

$$U(\omega) = \rho(r, \omega)\langle\nu\rangle\hbar\omega \quad (1)$$

The modal occupation number is summed over all modes of the structure. By examining the ratio of energy densities inside and outside the solar cell at thermal equilibrium, we can determine the maximum light intensity enhancement and thus the maximum light trapping that is possible.[1] We do this by taking the ratio of electromagnetic energy densities in two

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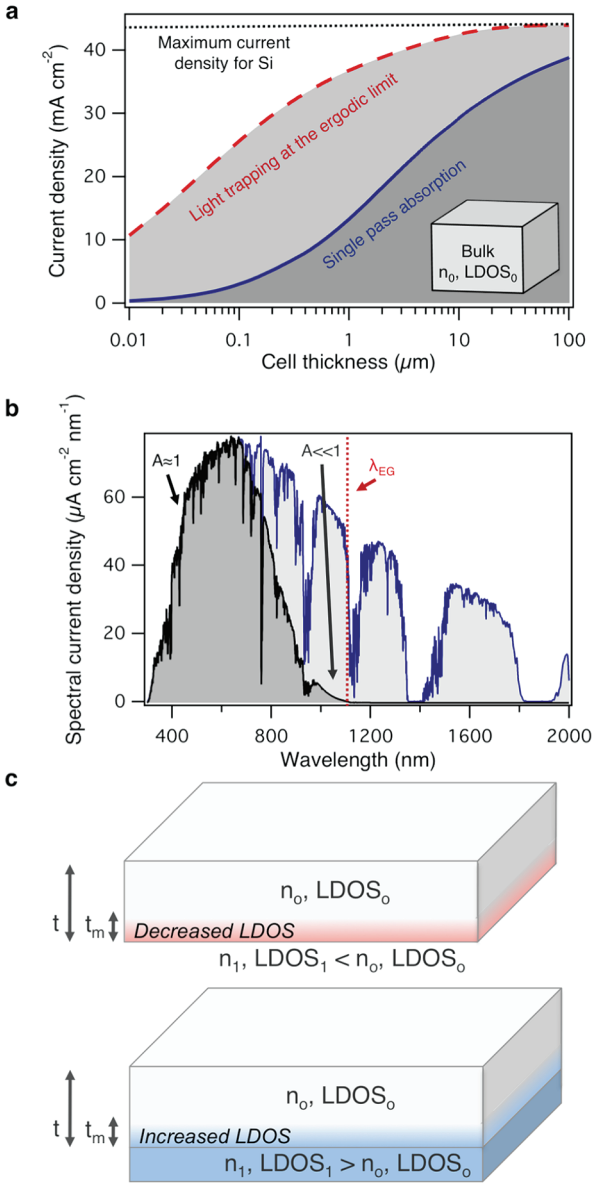

Figure 1. Traditional limits to photogenerated current. (a) Current density resulting from AM1.5 solar spectrum absorption for various thicknesses of a bulk slab of Si (inset) assuming either exponential absorption from a single pass or $4n^2$ passes at the ergodic light trapping limit. (b) Spectrally resolved absorbed current for a 100 nm slab of Si with light trapping at the ergodic limit. There is a significant region near the band edge where increased light trapping is needed beyond the ergodic limit. (c) A thin slab of semiconductor where the LDOS is affected by the surrounding environment.

distinct cases of interest. This gives an important ratio that includes the LDOS ratio and the modal occupation number ratio

$$\frac{U(r,\omega)_{\text{case1}}}{U(r,\omega)_{\text{case2}}} = \frac{\rho(r,\omega)_{\text{case1}}\langle\nu\rangle_{\text{case1}}}{\rho(r,\omega)_{\text{case2}}\langle\nu\rangle_{\text{case2}}} \quad (2)$$

This same ratio can be obtained from an expression for the local absorption rate with the energy density rewritten in terms of local fields (Supporting Information).

We can use this ratio to examine numerous cases of interest. In the limit of large thicknesses, we recover the ray optic light trapping limit for homogeneous materials (see Supporting Information). Here, we compare a homogeneous absorber with an arbitrarily designed absorber that may be capable of exceeding the ray optic light trapping limit:

$$\frac{\rho(r,\omega)_{\text{case1}}\langle\nu\rangle_{\text{case1}}}{\rho(r,\omega)_{\text{case2}}\langle\nu\rangle_{\text{case2}}} = \frac{\rho(r,\omega)_{\text{cell}}\langle\nu\rangle_{\text{cell}}}{\rho(\omega)_{\text{bulk}}\langle\nu\rangle_{\text{bulk}}} \quad (3)$$

where we have assumed integration over all modes of the structure. When an incoupling mechanism fully populates the modes of each structure, the light trapping enhancement is simply the LDOS ratio between the cell structure and a homogeneous bulk structure which achieves the ergodic limit (see Supporting Information for a further discussion of modal occupation). This implies that if the LDOS of the cell structure is larger than that of a homogeneous medium with the same refractive index, the ergodic light trapping limit can be exceeded. Inputting the expression for LDOS of a homogeneous medium with refractive index n, we reach the condition for exceeding the ergodic limit:

$$\frac{\pi^2 c^3}{n^3\omega^2}\rho(r,\omega)_{\text{cell}} > 1 \quad (4)$$

assuming that all modes of the structure are fully occupied via an appropriately designed light incoupler, which is often taken to be a Lambertian scattering surface.

We now outline a portfolio of wavelength-scale solar absorber layer designs that exhibit an LDOS modified relative to that of a homogeneous slab of the same material. We begin by examining ultrathin, planar solar cells for which we calculate the LDOS as a function of position within the semiconductor using the Green's dyadic for a layered planar system[11] and then integrate over position to get the spatially averaged LDOS. For the case of a finite thickness planar absorber, in Figure 1c, the LDOS modification can be viewed heuristically in terms a slab of thickness t with a homogeneous LDOS (LDOS_0) which is modified from its surface to some depth t_m by the LDOS of the neighboring material. In Figure 2, we plot this averaged LDOS enhancement for various absorber structures as a function of thickness and wavelength. When $t \gg 2t_m$, the absorber LDOS modification by the surrounding materials is negligible, but when $t \sim 2t_m$, the change in the absorber layer LDOS due to the influence of surrounding materials becomes significant. First, in Figure 2a we note that the integrated LDOS for a thin semiconductor slab surrounded by free space or lower index materials is always less than that of its corresponding bulk material as the slab thickness is reduced, implying that the light trapping limit in this structure is actually lower than that of the same material in bulk form. This has been pointed out before using a different methodology.[12] However, when the surrounding material includes a metal back-reflector as shown in Figure 2b, the integrated LDOS can exceed that of its corresponding bulk material in finite thickness layers, particularly for thicknesses below 200–300 nm. Further, the metal–insulator–metal (MIM) structure shown in Figure 2c exhibits an integrated LDOS enhancement relative to its corresponding bulk absorber material that is very significant for all thicknesses below ~500 nm, exceeding 50 for all relevant wavelengths with ultrathin layers below 20 nm.

For a two-dimensional planar structure, the modal density of states can be obtained from the optical dispersion relations. In this case, the density of guided modes per unit area per unit frequency for the mth mode can be written as[12]

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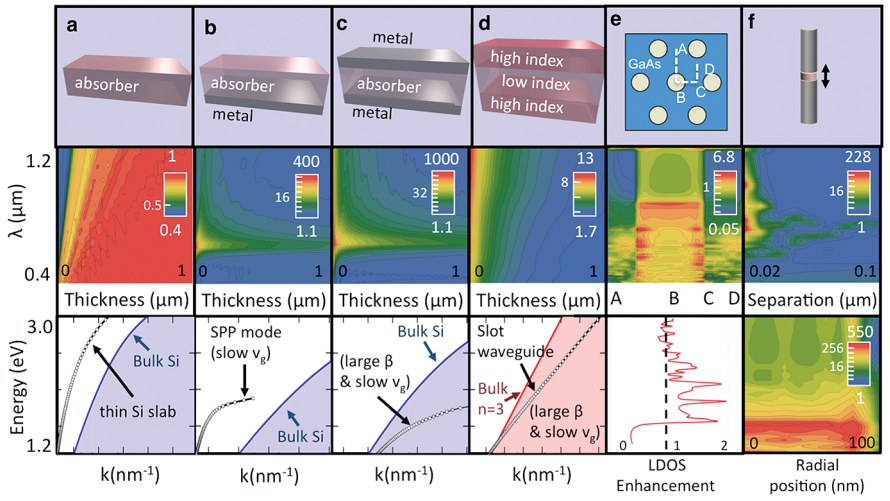

Figure 2. Potential solar cell architectures. (a) Planar slab of Si in air in which the LDOS is always below the bulk value. Structures with the potential to beat the ergodic limit. (b) Planar slab of Si on an Ag back-reflector, (c) Ag/Si/Ag planar structure, (d) high/low/high index structure with refractive indices 3/1.5/3, (e) a photonic crystal with index 3.7, and (f) a split dipole antenna made of Ag with a Si gap. The second row shows the LDOS enhancement (on a log color scale) over the bulk material for each structure for various cell thicknesses and wavelengths. Values of LDOS enhancement >1 correspond to beating the traditional absorption limit. For (a–d), the bottom row shows examples of the 2D modal dispersion curves for each structure. The bottom of column (e) shows that the integrated LDOS enhancement >1 in the photonic crystal for most wavelengths, and the bottom of column (f) shows the wavelength-dependent LDOS enhancement >1 for radial positions between the split dipole.

$$\rho_m = \frac{k_m}{2\pi}\left(\frac{d\omega}{dk_m}\right)^{-1} \quad (5)$$

where k_m is the propagation constant. In order to increase the density of modes above the homogeneous value, either $k_m > k_0$ or $v_m = d\omega/dk_m < v_0$, where k_0 and v_0 are the homogeneous values of the propagation constant and group velocity, respectively. Figure 2 also shows for each planar structure examples of the modal dispersion relations, showing regions where the density of states is increased due to either slow (low group velocity) modes or large in-plane propagation constants. Note that these plots do not fully depict the total LDOS due to the existence of multiple modes; however, many of the key features can be obtained from the dispersion relations. A full 2D waveguide formulation requires a slightly different analysis, which will be a subject of future work. For the metallodielectric structures, the plasmonic modes that contribute to the LDOS enhancement exhibit parasitic Ohmic metallic losses, and so exceeding the light trapping limit in any structure incorporating metals requires the "useful" absorption within the solar cell semiconductor absorber layer to dominate over parasitic metallic losses. This represents a challenge for successful implementation of certain cell designs incorporating metals, but we demonstrate below that it is possible to exceed the light trapping limit in metallodielectric structures with proper design.

A analogous planar structure without metallic losses is a dielectric slot waveguide[13] in which a low index absorber material is sandwiched between two nonabsorbing cladding layers of higher index, shown in Figure 2d for a core of dielectric constant 1.5 and a cladding of dielectric constant 3. The LDOS within the low index slot will be increased due to the presence of the high index cladding layers, which have an LDOS significantly higher than that for a bulk slab of the low index material. Over the entire range of the solar spectrum there is a significant integrated LDOS enhancement in the dielectric slot (Figure 2d). This effect can also be observed for common inorganic semiconductor materials such as GaP and CdSe (see Supporting Information). Similarly, dielectric slot waveguides have considerable potential as structures to achieve absorption enhancement in polymer and low index solar cells as there is no metallic loss mechanism. This phenomenon for similar structures has also been recognized in two recent works using different methodologies.[7,8]

Next we examine other structures with potential to exceed the light trapping limit. Photonic crystals[14] are interesting candidates as they are known to possess elevated LDOS around flat bands in their dispersive band structures. In Figure 2e, we show the LDOS calculated for a planar region within an ultrathin GaAs absorber layer with a photonic crystal on top of the absorber. This structure exhibits an integrated LDOS enhancement relative to a GaAs film over the wavelengths of interest above the semiconductor bandgap (see Supporting Information for additional details). Lastly, we point out that integrating solar cell absorber layers into an array of subwavelength-scale optical cavities also offers a prospect of large LDOS and absorption enhancement beyond the ray optic limit. As an example, we calculate the LDOS within the gap of a metallic split dipole nanoantenna, shown in Figure 2f. The LDOS enhancement is large and relatively broadband due to the hybridization of each of the monomer resonances and the low quality factor of the antenna. This structure allows for a large degree of tunability of the resonance wavelength, the LDOS peak enhancement, and bandwidth by tuning the antenna length/diameter ratio (see Supporting Information for additional details). Of course, it is also possible to design all-dielectric cavities of this type.

Figure 3 shows the density of states enhancement needed to absorb 99.9% of the solar spectrum for various thicknesses of Si and GaAs. For ultrathin layers we find that the density of states enhancement needed is very reasonable, especially in the context of the above results. It is thus possible to imagine absorbing nearly the entire solar spectrum with ultrathin layers of semiconductors as thin as 10–100 nm. The most important criterion that gives an upper bound to the absorbance of a solar cell absorber layer is the extent to which the density of states

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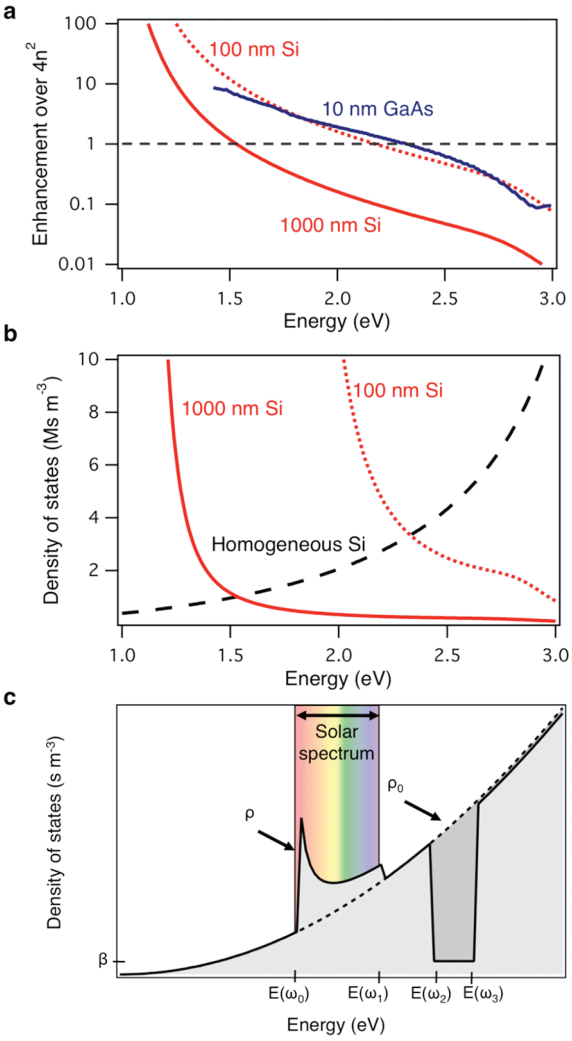

Figure 3. Enhancements needed to absorb the entire solar spectrum. (a) Absorption enhancement over $4n^2$ (proportional to LDOS enhancement over the homogeneous value) for various thicknesses of Si and GaAs needed to fully absorb the AM1.5 solar spectrum. (b) Needed density of states profiles for two thicknesses of Si needed to fully absorb the spectrum. (c) Schematic of spectral reweighting needed to achieve density of states enhancements.

can be raised in the wavelength range where absorption is required. This upper bound is determined by the density of states sum rules,[15] which dictate that as the density of states is increased in a region of the spectrum, then it must decrease in another region of the spectrum so as to satisfy

$$\int_0^\infty \frac{\rho_{cell} - \rho_{vac}}{\omega^2}\, d\omega = 0 \qquad (6)$$

We show in Figure 3c how this spectral reweighting could occur to allow a density of states enhancement in the desired region of the spectrum. Spectral reweighting occurs naturally whenever a change in the density of states occurs but can potentially be artificially engineered at will with clever tuning of dispersion using photonic crystals or metamaterials, for example. Thus, the density of states could potentially be enhanced to a reasonably large value which is limited by the bandwidth of the spectral reweighting region (see Supporting Information). Since the bandwidth of needed enhancement is limited (i.e., the solar spectrum) and the region from which we can afford to decrease the density of states is nearly unlimited (i.e., regions outside of the solar spectrum), we expect other physical and practical limits to be relevant before a limit is reached for increasing the density of states, such as saturated absorption in the active layer or device and processing issues with extremely thin devices.

As a simple proof-of-principle, we perform three-dimensional electromagnetic simulations using finite difference time domain methods for two test structures using the measured optical properties of real materials that demonstrate these concepts. Figure 4 shows the fraction of incident illumination absorbed

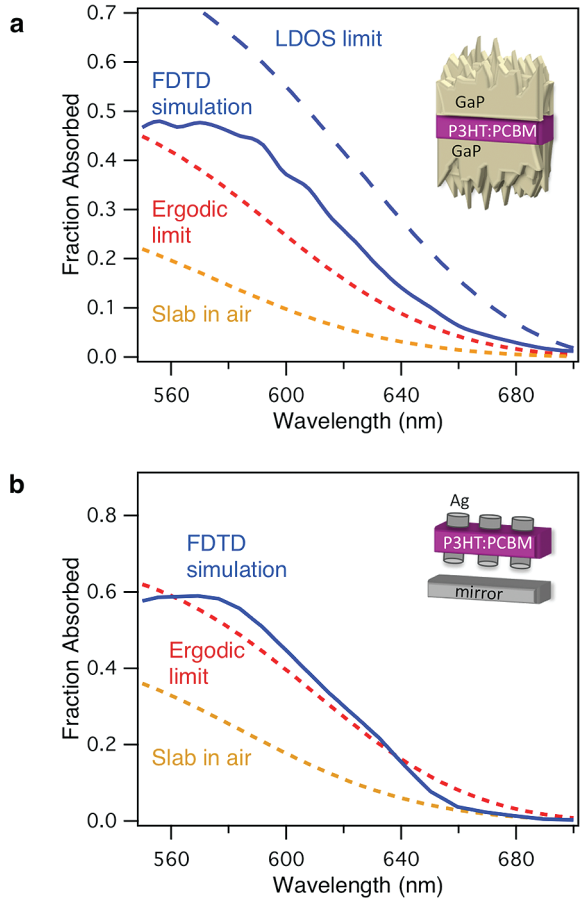

Figure 4. Structures that surpass the ergodic limit. Full-wave simulations of a P3HT:PCBM structure cladded with (a) roughened GaP or (b) plasmonic resonators with absorption enhancement exceeding the ergodic limit. The absorption greatly exceeds the LDOS limit for the slab of P3HT:PCBM in air (dashed orange line) and approaches the LDOS limit for the P3HT:PCBM slot (dashed blue line) with refined incoupling.

by a 10 nm layer of P3HT:PCBM, a common polymeric photovoltaic material for both a dielectric slot waveguide (Figure 4a) and a hybrid plasmonic structure (Figure 4b). For the slot waveguide, the P3HT:PCBM layer is cladded on both sides by 500 nm of roughened GaP, a high index material with little to no loss in the wavelength range of interest owing to its indirect bandgap at 549 nm. In this structure, the elevated LDOS leads to an enhancement of the absorption that exceeds the ray optic light trapping limit even without equal population of all of the modes of the structure at all wavelengths where the GaP cladding is transparent. This structure exceeds both the $2n^2$ and $4n^2$ limits (Supporting Information) for absorption

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enhancement without and with a back-reflector, respectively. Ideally, Lambertian scattering surfaces could be designed to allow more nearly equal incoupling to all of the modes, which will further enhance the absorption over the entire range of the spectrum to the new limit shown by the blue dashed line in Figure 4a. We also calculate the LDOS limit for this slab in air (orange dashed line), which is exceeded by our simulation for all wavelengths. For isotropic illumination, the angle-averaged absorption also surpasses the ray-optic limit (see Supporting Information). Similarly, Figure 4b indicates that plasmonic resonators situated above and below the absorber layer also enable absorption enhancements that surpass the ergodic limit (We do not show the LDOS limit line in Figure 4b because we do not expect to reach it due to metallic loss in the structure). These two examples demonstrate that with proper design of LDOS and incoupling the ergodic limit can be exceeded in several different ways.

We have identified the local density of optical states as a key criterion for exceeding the ray optic light trapping limit in solar cells. To exceed the ray optic limit, the absorber must exhibit a local density of optical states that exceeds that of the bulk, homogeneous material within the active region of the cell. In addition to this, the modal spectrum of the device must be appreciably populated by an appropriate incoupling mechanism. We have outlined a portfolio of solar absorber designs that can meet the LDOS criterion implemented utilizing plasmonic materials, dielectric waveguides, photonic crystals, and resonant optical antennas, and examples are given to show that incouplers can be designed that provide appreciable mode population. These concepts and design criteria open the door to design of a new generation of nanophotonic solar cells that have potential to achieve unprecedented light trapping enhancements and efficiencies.

■ ASSOCIATED CONTENT

Supporting Information

Theoretical details and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Yablonovitch, E. Statistical ray optics. *J. Opt. Soc. Am.* **1982**, *72* (7), 899−907.

(2) Atwater, H. A.; Polman, A. Plasmonics for improved photovoltaic devices. *Nature Mater.* **2010**, *9* (3), 205−13.

(3) (a) Garnett, E.; Yang, P. Light Trapping in Silicon Nanowire Solar Cells. *Nano Lett.* **2010**, *10* (3), 1082−1087. (b) Kelzenberg, M. D.; Boettcher, S. W.; Petykiewicz, J. A.; Turner-Evans, D. B.; Putnam, M. C.; Warren, E. L.; Spurgeon, J. M.; Briggs, R. M.; Lewis, N. S.; Atwater, H. A. Enhanced absorption and carrier collection in Si wire arrays for photovoltaic applications. *Nature Mater.* **2010**, *9* (3), 239−244.

(4) Han, S. E.; Chen, G. Toward the Lambertian Limit of Light Trapping in Thin Nanostructured Silicon Solar Cells. *Nano Lett.* **2010**, *10* (11), 4692−4696.

(5) Chutinan, A.; Kherani, N. P.; Zukotynski, S. High-efficiency photonic crystal solar cell architecture. *Opt. Express* **2009**, *17* (11), 8871−8878.

(6) Saeta, P. N.; Ferry, V. E.; Pacifici, D.; Munday, J. N.; Atwater, H. A. How much can guided modes enhance absorption in thin solar cells? *Opt. Express* **2009**, *17* (23), 20975−20990.

(7) Yu, Z. F.; Raman, A.; Fan, S. H. Fundamental limit of nanophotonic light trapping in solar cells. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107* (41), 17491−17496.

(8) Green, M. A. Enhanced evanescent mode light trapping in organic solar cells and other low index optoelectronic devices. *Prog. Photovoltaics* **2011**, DOI: 10.1002/pip.1038.

(9) Zhu, J.; Yu, Z.; Fan, S.; Cui, Ti Nanostructured photon management for high performance solar cells. *Mater. Sci. Eng. R* **2010**, *70*, 330−340.

(10) (a) Gee, J. M. Optically enhanced absorption in thin silicon layers using photonic crystals. *29th IEEE PVSC Proc.* **2002**, 150−153. (b) Sheng, P.; Bloch, A. N.; Stepleman, R. S. Wavelength-selective absorption enhancement in thin-film solar cells. *Appl. Phys. Lett.* **1983**, *43*, 579.

(11) (a) Barnes, W. L. Fluorescence near interfaces: the role of photonic mode density. *J. Mod. Opt.* **1998**, *45* (4), 661−699. (b) Ford, G. W.; Weber, W. H. Electromagnetic-Interactions of Molecules with Metal-Surfaces. *Phys. Rep.* **1984**, *113* (4), 195−287. (c) Novotny, L.; Hecht, B. *Principles of Nano-optics*; Cambridge University Press: Cambridge, 2006; p xvii, 539 pp.

(12) Stuart, H. R.; Hall, D. G. Thermodynamic limit to light trapping in thin planar structures. *J. Opt. Soc. Am. A* **1997**, *14* (11), 3001−3008.

(13) Almeida, V. R.; Xu, Q. F.; Barrios, C. A.; Lipson, M. Guiding and confining light in void nanostructure. *Opt. Lett.* **2004**, *29* (11), 1209−1211.

(14) (a) Joannopoulos, J. D. *Photonic Crystals: Molding the Flow of Light*, 2nd ed.; Princeton University Press: Princeton, 2008; p xiv, 286 pp. (b) Yablonovitch, E. Inhibited Spontaneous Emission in Solid-State Physics and Electronics. *Phys. Rev. Lett.* **1987**, *58* (20), 2059−2062.

(15) (a) Barnett, S.; Loudon, R. Sum rule for modified spontaneous emission rates. *Phys. Rev. Lett.* **1996**, *77* (12), 2444−2446. (b) Scheel, S. Sum rule for local densities of states in absorbing dielectrics. *Phys. Rev. A* **2008**, *78*, 013841.