Complex Photonic Structures for Light Harvesting

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Over the last few years, micro- and nanophotonics have roused a strong interest in the scientific community for their promising impact on the development of novel kinds of solar cells. Certain thin- and ultrathin-film solar cells are made of innovative, often cheap, materials which suffer from a low energy conversion efficiency. Light-trapping mechanisms based on nanophotonics principles are particularly suited to enhance the absorption of electromagnetic waves in these thin media without changing the material composition. In this review, the latest results achieved in this field are reported, with particular attention to the realization of prototypes, spanning from deterministic to disordered photonic architectures, and from dielectric to metallic nanostructures.

1. Introduction

Sunlight has by far the highest theoretical potential of the Earth's renewable energy sources. The solar constant (the solar flux intercepted by the Earth) is 1.37 kW m$^{-2}$. Taking into account the cross-sectional area of the Earth intercepting this flux, losses by atmospheric scattering or absorption, and other relevant factors, the available solar power is 89 300 TW. This theoretical potential represents more energy striking the Earth's surface in 2.5 h than the worldwide energy consumption in the year 2013 from all sources combined.\(^{[1]}\) This theoretical potential could be used to generate 15 TW of carbon-neutral power (the target value for year 2050, which is believed will stabilize atmospheric CO$_2$ values) from 10% efficient solar-conversion systems covering only 0.17% of the Earth's surface area.\(^{[2]}\) For a country like the USA, the potential solar energy from the surface covered by public roads equals roughly the total energy need of the country. Currently, this potential remains largely unused, with photovoltaic energy sources covering less than 0.1% of the global energy needs.

A worldwide adaptation to solar energy sources could be favored by improving solar cell efficiency and hence lowering the material needs and costs. Photonic techniques can play an important role by increasing the capabilities of a material to trap light, thus facilitating absorption. Ideally, one wants to maximize the coupling of light into a structure while minimizing the amount of light that escapes. In an absorption-free medium, this requirement is in contrast with reciprocity in Maxwell's equations, but it is allowed in a material with non-negligible absorption. In the ideal situation, light should easily enter, but then remain as long as possible inside so that efficient absorption and conversion from light to electricity can take place.

In the field of solar cell applications, a planar geometry is usually employed, where the system is much wider than it is thick. This geometry is dictated by the need of intercepting as many photons as possible while keeping the building material to a minimum. The reason for the latter is not only cost-effectiveness. In general, photogenerated charge carriers drift once they are in proximity of the electrostatic field of the p–n junction; however, when they are far from it they diffuse for a particular length—the so-called minority carrier diffusion length—after which they recombine with holes, dissipating their kinetic energy as heat. Hence, the ultimate goal is to make the material as thin as possible while still maintaining good absorption characteristics: indeed when the film is too thin, part of the light is transmitted and, thus, lost. The role of photonic structures is then to make the material optically thick, by coupling light into the so-called guided modes of the thin film, to ‘store’ it for long enough to allow a relevant absorption to occur. Ideally, the coupling mechanism should work efficiently for any direction of incident light. This holds well if there is a high density of optical modes in the plane of the structure with, at the same time, a certain amount of coupling between these modes and the free space outside.

In past years, several nanophotonic strategies have been proposed, and nowadays the field is mature enough for the fabrication of prototypes. This is a delicate matter, since the realization of photonic nanostructures demands a significant modification of the cell surfaces and crystalline bulk structures, which is generally detrimental for the transport properties of electrons. In essence, improved light absorption would be worthless if it is not followed by a net increase of current generation. Hence, in this review, we will focus on the latest results in the literature with particular interest in those studies concerning the realization of photonic-nanostructured solar cell prototypes. The manuscript is structured into two main sections:
i) deterministic photonic structures (a morphology that can be designed by a specific mathematical rule), and ii) the emerging disordered photonic structures (a morphology that can be designed by statistical principles). These two sections will consider both dielectric and metallic photonic architectures. At the end of the manuscript a Glossary Section has been included to help the reader with the technical terminology.

2. Deterministic Photonic Structures

2.1. Deterministic Dielectric Photonic Structures

The refractive index contrast between air and the dielectric material of the cell is often pronounced, leading to a relevant reflection of light at the cell interface, which reduces light absorption. This effect becomes more important for large incidence angles, as predicted by the Fresnel equations. In the past decades, various approaches have been exploited to fabricate broadband all-angle antireflective structures. Simpler ones, e.g., textures on bulk silicon devices, are based on a ray optics approach. Others obtain constructive interference inside the absorbing film, exploiting single or multiple index-matched layers with thicknesses on the order of a quarter of a wavelength. Coatings based on graded refractive index front layers have also been developed. Such structures are composed by successive layers with an optical thickness increasing according to a polynomial law. In this respect, 1D or 2D patterns have also been successfully implemented on the front surfaces of solar cells.

Light with an energy close to the electronic band edge of the active material is scarcely absorbed, especially in the case of thin-film devices whose absorption lengths are longer than the thickness of the cell. Generally, in this case, absorption enhancement is achieved by developing strategies to increase the optical path inside the material, often achieved by exploiting total internal reflection. Theoretical limits for the possible optical path enhancement of bulk architectures have long been established to be 4π for unpolarized light in the ray optics approximation. Such a limit has been extended in the past few years to light-trapping approaches, where the wave nature of light is dominant, e.g., in thin-film materials. Given the demand for efficient and cost-effective energy-harvesting devices, thin-film devices have been considered, offering the potential to reduce the use of expensive materials and to fully exploit advanced photonic light-trapping approaches. Such methods not only involve structures placed on top or behind the dielectric layer(s), but they can themselves be realized within the active materials. In contrast to previous architectures based on geometric optics, these structures fully exploit the wave nature of light, thus storing light inside the material for long time. This translates into a pronounced absorption enhancement. Furthermore, the local density of photonic states can be tailored to accomplish a pronounced energy harvesting.

2.1.1. Structures Based on Ray Optics

The market of solar cells is currently dominated by bulk silicon devices. For these systems, texturing of sizes much larger than the incident wavelengths have been employed, trying to enhance the absorption in the infrared part of the spectrum and to reduce the amount of expensive materials. Different shapes and aspect ratios were considered for texturing. A recently proposed concept considers inverted pyramids, at the facet of which light experiences multiple reflections (see Figure 1a). The probability of light being absorbed is thus enhanced as compared to a simple flat surface, where light is immediately back-reflected into the environment. With this method, a power conversion efficiency as high as 24% has been demonstrated and scaled to mass production.

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The development of structures performing wide-angle acceptance and designed according to ray optics concepts is still under consideration due to the recent advancements of fabrication techniques. Micro lenses, for example (Figure 1b), focus the light incident from large angles inside the active layer. Texturing placed above the active layer is advantageous because it avoids possible damage of the film during fabrication. In addition, microlenses have been suggested as a valid solution to reduce the shading of front metallic contacts. Devices with active layers made of high refractive-index materials, e.g., crystalline silicon, have been proven to strongly benefit from the presence of periodic modulations on their front or back surfaces. Here, we focus on the main physical mechanism for light scattering from an ideal transmissive 1D dielectric grating, as described by the diffraction equation:

\[ n_1 \sin \theta_1 - n_2 \sin \theta_2 = \frac{m \lambda}{d} \quad (1) \]

where \( n_1 \) and \( n_2 \) are the indices of refraction of the air and the dielectric material of the layer, respectively, \( d \) is the period of the grating and \( \lambda \) is the incident wavelength. The incident angle is \( \theta_1 \), \( \theta_2 \) is the diffracted angle, and \( m \) is the diffraction order. While for small periods (\( d < \lambda/n_2 \)) only the lowest order is excited, for \( d > \lambda/n_2 \) light can be diffracted into the film with an angle that satisfies total internal reflection, thus trapping light in guided modes. The shape of the grooves comprising the structure is related instead to the intensity delivered to the various diffractive orders. For this reason, different shapes have been considered, such as rectangular or triangular grooves in mono-periodic gratings, and direct or inverted pyramids, cones, and holes in planar ones. When the real shape of the scattering objects is taken into account and the periodicity of the gratings becomes comparable to the wavelength, advanced numerical modeling such as rigorous coupled wave analysis becomes necessary.

Given the relative simplicity of grating theory and the high-level expertise reached by the fabrication methodologies nowadays, several studies on solar cell prototypes have been published. For example, through nanoinprint techniques, Chen et al. fabricated a grating structure of inverted pyramids in a conjugated polymer layer, namely, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), on a c-Si wafer substrate. Such a polymer material is transparent and is able to form a radial Schottky junction with n-type silicon. These devices are interesting due to the cheap materials employed, the fabrication technique, and the particular junction topology which improves the internal quantum efficiency for all the frequency ranges (300–1100 nm). All-back-contact architectures have also been considered in combination with front-side light-trapping structures. Jeong et al. successfully implemented nanocones of 450 nm and height 400 nm on a 10 µm-thick c-Si active layer. The external quantum efficiency, that is, the ratio of extracted charge carriers to the number of photons in the incident beam, was found to be above 80% in the range 400–800 nm. A power conversion efficiency of 13% was obtained, overcoming the 10% result of the nonpatterned cell.

### 2.1.2. Grating Structures

The idea of exploiting the wave nature of light to enhance the efficiency of solar cells using diffractive grating structures was suggested long ago. Devices with active layers made of high refractive-index materials, e.g., crystalline silicon, have been proven to strongly benefit from the presence of periodic modulations on their front or back surfaces. Here, we focus on the main physical mechanism for light scattering from an ideal transmissive 1D dielectric grating, as described by the diffraction equation:

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### 2.1.3. Thin-Film Solar Cells

Thin-film materials could open the way to low-cost solar cells. The reduced thickness of the active material has a beneficial effect on photogenerated charge collection, reducing the distance between contacts. Unfortunately, it concurrently affects the absorptive capability of the system, since most of the light with energy at the edge of the electric bandgap of the material will only be minimally absorbed. For this reason, light-trapping structures become crucial in thin-film devices. However, from a design viewpoint, when using gratings with periodicity (\( L \)
comparable with the incident wavelength ($\lambda$) on top of films with a thickness close to $\lambda$, grating theory is no longer accurate. Under such conditions, interference effects take place, and a theoretical description taking into account wave optical effects is necessary. A statistical temporal coupled-mode theory\[^{44}\] has been successfully used to calculate an upper limit for absorption enhancement in these structures.\[^{12}\] It has been shown that deterministic nanophotonics structures are expected to significantly exceed the standard absorption enhancement limit, $4n^2$ —also known as the Yablonovitch limit\[^{45}\]—which has been derived for bulk low-absorbing structures with roughened surfaces, giving rise to Lambertian scattering (see Section 3.1 below). In this model, the absorption of the system is proportional to the number of resonances $M$ (Figure 4a–c) corresponding to frequencies that are able to couple to guided modes in the thin film, and inversely proportional to the number of channels $N$ available in free space. Let us consider the case of 2D gratings above a bulk absorbing film. In this condition, only light with a wave vector $k = m2\pi/L$ with $m = 0, \pm 1, \pm 2, \ldots$ can be used to excite the modes in the film and, concurrently, only modes with $k \leq k_0 = w/c$, where $w$ is the frequency and $c$ the speed of light—the so-called light line—can be excited from outside (Figure 4b). When $L = \lambda$, there is only one channel with several resonances, leading to an absorption enhancement exceeding the classical limit (Figure 4d).

For ultra-thin films, that is, when the thickness is half the incident wavelength or smaller, it can be shown that, to fully exploit the nanophotonics capabilities, the designed structures must yield deep-subwavelength field confinement and/or low group velocity.\[^{12}\] The fabrication of 1D or 2D gratings has been implemented in solar cells using different active materials.\[^{38,46–48}\] Glass nanograting structures on a-Si:H, for example, have been recently investigated (see Figure 5).\[^{49}\] By introducing a light-trapping structure, the authors succeeded in enhancing the short-circuit current density and the power conversion efficiency of the device up to 50%, while leaving the other electrical parameters such as the open-circuit voltage $V_{oc}$ and the Fill Factor (FF)\[^{10}\] primarily unaffected. The effect of light-trapping structures on polymeric solar cells is currently under investigation.\[^{8,50–53}\] Cheng et al.\[^{71}\] for example, used capillary force lithography to imprint a regular grating on the transparent conductive oxide (TCO) layer, or directly in the active layer, of an inverted organic solar cell (Figure 6a). Even if more efficient solar cells have been fabricated with polymeric materials,\[^{52}\] the introduction of nanostructures into the active layer results in a 27% increase of the power conversion efficiency (Figure 6b). This shows the suitability of capillary force imprint techniques for the fabrication of photonic structures in these devices, preventing the deterioration effects that typically affect standard imprinting methodologies.

A further relevant characteristic of light-trapping structures in thin-film solar cells is their nontrivial angular response.\[^{53,54}\] Investigations of this aspect are crucial in view of the fact that the operation of these devices occurs at an oblique incidence for most of the time. From a photonic point of view, an increase of the incidence angle corresponds to a shift of the wave vectors of the grating in the reciprocal space. An angular characterization of the external quantum efficiency has been recently performed for amorphous silicon solar cells, where monopериodid sine-shaped grating structures were fabricated on the front surface.\[^{60}\] They estimated for wavelengths in the range 590–750 nm and unpolarized light a short-circuit current density enhancements of 20% larger than what is expected with Lambertian roughening. The effect of the modal dispersion on the external quantum efficiency was obtained experimentally, and compared with numerical calculations (Figure 7).

Since the optical behavior of microgratings and photonic structures on thin films has been studied quite extensively in the past years through numerical calculations,\[^{55–58}\] their full exploitation in real devices is currently under investigation.\[^{39,59–62}\] Depauw et al.\[^{58}\] fabricated a periodic pattern of...
holes on the front surface of a 1 µm-thick crystalline silicon solar cell. The TCO layer on the front of the cell has the same morphology of the photonic crystal etched in the silicon layer (Figure 6c,d). A topological, optical, and electrical characterization was performed on the samples to identify the effect of this structure on charge collection. Significant enhancements of the short-circuit current density up to approximately 20% have been measured for angles up to 60°. Unfortunately, the patterning induces a significant reduction of the $V_{oc}$, and quantum efficiency measurements suggest an increase in surface recombination, which in turn decreases the overall efficiency of the device.

2.1.4. Aperiodic Photonic Structures

Up to this point, we have considered solar cell architectures with periodic light-trapping patterns. However, the absorption enhancement obtained with this approach usually takes place in relatively small frequency bandwidths. Interests has recently been devoted to other types of deterministic structures achieved, for example, by modifying the structural properties of the system in such a way as to reach an intermediate optimal response. One of the more straightforward strategies is the introduction of controlled defects in photonic crystals, which results in a so-called superlattice. This method leads to the creation of additional modes that propagate in the structure, and thus yield richer resonance spectra. The local density of states of photons can be manipulated as well as the in-coupling with the absorbing structure (Figure 8).

In the literature, a few works can be found exploring the possibility to exploit nonperiodic deterministic structures—that is, without translational invariance—to improve the optical response of thin-film solar cells. These systems are usually generated by some substitution rule of two elementary objects, e.g., two values of the dielectric constant or two different thicknesses (1D), or radii (2D). A subset of these, quasi-crystals, can be generated through projections of periodic structures from higher dimensions and present long-range ordered features. The interest in these structures for light management lays in the control of their structural order at different length scales and the exploitation of noncrystallographic symmetries. Their high-order rotational symmetries, compared to periodic ones, is a crucial characteristic to have both enhanced scattering angles and broader wavelength response. Indeed, the order of local rotational symmetry is closely related to the number of nearest neighbors of each scatterer and, more generally, to how evenly the points in the pattern spread out in space. These properties are studied from the Fourier transform of the positions of the scattering elements in real space, also known as the structure factor $S(k)$. With respect to the in-coupling mechanism for periodic structures, quasi-crystal structures have a denser spectrum in reciprocal space, resulting in a larger probability of satisfying the matching condition for in-coupling. As a consequence, quasi-crystalline structures can enhance the absorption as much as periodic ones, but with a more isotropic angular response.

Figure 3. a) Optical image of the back (top, left) and front (top, right) of a 10 mm-thick Si solar cell. SEM images of cross-sectional view of the device (bottom, left) and cross-sectional view of the nanocones (bottom, right). b) Schematic illustration of the device. c) External quantum efficiency data of the device. d) $J–V$ characteristics of the two devices in (c). Reproduced with permission. Copyright 2013, Macmillan Publishers Ltd.
Numerical calculations have been performed on quasicrystal patterns of various symmetries, and their light-trapping performance has been compared with other strategies involving periodic \cite{71,72} and disordered structures. \cite{67,73,74} Quasi-crystalline structures have also been practically realized with nanoimprint lithography (NIL), or focused ion-beam (FIB) milling (Figure 9), \cite{67,74–77} and have been implemented as architectures for solar cells. \cite{78,79}

2.2. Deterministic Plasmonic Structures

In metals, nanophotonics is subject to different optical phenomena, since conducting electrons are free to move when an electric field is applied. As a result, a slowly (<1 THz) varying electromagnetic wave forces these electrons to oscillate. In the simplified model of Drude, \cite{80} the electrons are considered to move 180° out of phase with respect to the driving field, effectively “screening” the interior of the metals and eventually creating a volume of vanishing electromagnetic field. However, electrons move with a finite velocity, so when the field varies faster than their response, the electric field can penetrate the metal to a minute depth. The length of this depth becomes more and more pronounced as the electromagnetic frequency approaches the so-called plasma frequency, which varies according to the material properties. At optical frequencies, metals sustain surface charge density oscillations, to which light can couple, giving rise to surface plasmon polaritons (SPPs), which can be considered electromagnetic waves bound to the metal surface. Since SPPs are oscillations of electrons in a material with finite conductivity, they can be described as damped waves and, thus, they are always subject to absorption. Let us consider the interface (parallel to the x axis) between a metal ($\varepsilon_m$) and a dielectric ($\varepsilon_d$). The dispersion relation of an SPP is:

$$k_x = k_0 \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}$$

(2)

where $k_0$ is the wavevector in a vacuum. According to the Drude model,

$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}$$

(3)

where $\omega_p$ is the plasma frequency and $\Gamma$ is the damping rate, which takes into account the absorption of the metal. When $\varepsilon_m < -\varepsilon_d$ (this condition defines the so-called SPP
resonance), it turns out that $k_x > k_0$ and, thus, SPPs are trapped at the metal interface, with its intensity exponentially decaying from the interface. In the limit of lossless metals (perfect metals), $k_x$ is purely imaginary and, thus, no propagating SPPs can be sustained. This corresponds to the case of very low-frequency electromagnetic fields, for which the metal is nearly perfect.

The most striking property of SPPs is the possibility to concentrate light beyond the diffraction limit. Surface plasmon polariton modes, sustained on nanowaveguides with diameters much smaller than the plasmon wavelength, have been repeatedly reported. As it has been argued, this can be seen as a concentration of electromechanical, rather than electromagnetic, energy. The energy of the system is thus the sum of the potential and mechanical kinetic energies of the free electrons, as proposed in the Drude–Sommerfeld model. This field concentration is not due to interference effects of multiply scattered waves, as in the case of dielectric nanophotonic structures (see Sections 2.1 and 3.1), and thus it is not bound to the Abbe diffraction limit. Strong light confinement leads to larger field enhancement, which can be exploited to locally increase the light absorption of materials in the vicinity of metals, with evident advantages for photovoltaic applications. Such a field enhancement, however, comes with a cost. As the field is more concentrated, it penetrates further into the metal, which is a lossy material. In order to use SPPs for photovoltaics, a careful trade-off between field concentration and metallic absorption has to be found by properly choosing the materials employed and tailoring the metal surfaces. Surface tailoring at the nanoscale is necessary not only to concentrate SPPs, but also to excite them. Being waves bound to the surface of a metal, SPPs exhibit a momentum mismatch with free propagating light (as discussed above), which is generally circumvented by nanostructuring the metal surface, for example, with gratings.

2.2.1. Gratings and SPPs

Since the realization of the first solar cell prototypes, their back contact has been made of metal. Although there is nowadays a large variety of proposed architectures for solar cells, involving both organic or solid state solutions, most of them still use...
metal back contacts. As the demand for thinner active layers increased, it became natural to try to introduce some kind of corrugation in this metal film to scatter light parallel to the thin active layer. The initial solutions were to realize either a disordered texturing of the metal film, achieving a Lambertian scattering of light, or periodic patterns, i.e., gratings, which scatter light at specific angles. Some of these angles are beyond the critical angle for total internal reflection, for which the absorption length of the active layer is longer. For shorter wavelengths, in thin films made, for instance, from µc-Si, a-Si, CdTe, and other solid state materials, the absorption length is much shorter than its thickness, thus, no light-trapping mechanism is required.[86,87] For ultrathin films, generally used in so-called third-generation solar cells, the thickness of the active layer is sub-micrometric, sometimes less than 200 nm. Trapping light by photonic means (see Section 2.1) in such a thin active layer leads to several difficulties. Firstly, the presence of the back contact metal gives rise to a cut-off frequency for the guided modes of the film, preventing light trapping at relatively long wavelengths. Secondly, a significant percentage of the total intensity of the guided light is not confined to the active region, especially for the low-refractive-index organic solar cells, thus decreasing the absorption efficiency. Under such conditions, the presence of SPPs can significantly increase solar cell performance. SPP modes do not suffer from a frequency cut-off. In addition, the intensity of an SPP is strongly enhanced in the vicinity of the metal, i.e., very close to the active layer. These enhanced plasmon-trapping effects come at the cost of losses due to the metal absorption, which dissipates energy as heat. With the proper choice of materials and their geometry it is possible to find the best trade-off between reduced plasmon losses and pronounced field confinement. Plasmonic architectures are predicted to significantly increase the performance of ultrathin solar cells, both solid state and organic,[88] and several prototypes have been already realized and investigated.[89–92] Ferry and co-workers[93] developed a plasmonic solar cell based on a 2D grating which shows a 26% (see Figure 10) enhancement in short-circuit current density. This was obtained by using active layers of less than 200 nm, for which optical guided modes are not supported, exploiting the coupling to SPPs at the metal interface. Furthermore, the device was fabricated by nanoimprint lithography, which is a relatively cheap, large-area fabrication method, showing that plasmonic nanostructures are promising also for industrial implementation.

2.2.2. Complex SPP Architectures

More sophisticated solutions have been investigated in the last years regarding the evolution of gratings. Modified gratings...
have been proposed and are expected to improve absorption in thin-film materials due to the combination of grating properties and the plasmonic field enhancement capabilities.\cite{94} Gratings with inclusions or indentations have been also considered to significantly rise the absorption of, for instance, organic materials.\cite{95, 96} The general idea is to combine the coupling properties of a metallic grating with the field enhancement occurring when two metal interfaces are in very close proximity (see Section 3.2). In such a configuration, not only is light trapped in SPP modes, but its intensity is also strongly localized in the active material between the metals and thus efficiently

![Figure 8](image1.png)

**Figure 8.** a) Two different superlattice geometries and their spectral absorption b) as a function of superlattice air hole diameter. For reference, the vertical dotted white lines indicate when the superlattice air hole diameter is the same as the background lattice air hole diameter (i.e., no superlattice). c) Absorbed current as a function of superlattice air hole diameter for four different configurations obtained by integrating the spectral absorption and weighting by the AM 1.5 solar spectral current. Reproduced with permission.\cite{15} Copyright 2012, the American Chemical Society.

![Figure 9](image2.png)

**Figure 9.** a) Moiré nanolithography as described in.\cite{75} (Reproduced with permission.\cite{75} Copyright 2012, the American Chemical Society). Fabrication scheme of moiré patterns from a hexagonal mask exposed twice at an angular offset $\alpha$. SEM images and (insets) Fourier transforms of the first-order Bragg peaks for b) a hexagonal array ($\alpha = 0^\circ$), c) a superperiodic array ($\alpha = 10^\circ$), d) a superperiodic array ($\alpha = 20^\circ$), and e) a 12-fold array ($\alpha = 30^\circ$). f) Absorption spectra for the optimized periodic and quasi-periodic structures. The AM 1.5 solar spectrum (magenta-dotted) and the absorption spectrum of the solar cell with a silver mirror as a back-reflector (black-dotted) are also shown. g) Absorption enhancement versus incident angle for optimized periodic structures. Reproduced with permission.\cite{71} Copyright 2013, AIP Publishing LLC.
absorbed. By engineering the hybridization of the localized SPP and the SPP modes in nanovoids, Lee and co-workers \cite{95} introduced a tunable resonance into the absorption spectra. They firstly adjusted a standard grating design in order to achieve a 33% relative absorption enhancement (see Figure 11). They then introduced an indentation in the grating which gives rise to an absorption resonance in the NIR, leading to a 41% relative absorption enhancement.

Surface plasmon polaritons can be launched also by approaches other than gratings.\cite{97} Ferry et al.\cite{98} proposed to enhance the absorption of a thin-film material, fabricating an array of grooves in a metallic back contact (Figure 12). Each groove efficiently couples the solar radiation to SPPs due to their large scattering cross-section. These nanoindentations are arranged in a periodic manner, in order to homogeneously cover the film. The distance between grooves was chosen depending on the SPP absorption length and their orientation was designed so to have an efficient scattering for different polarizations. The advantage of such a configuration is that the incident angular dependency of the relative absorption enhancement (reported to be 150%) is extremely minute.

A different kind of periodic plasmonic nanostructure which has been investigated for harvesting the solar radiation impinging on ultra-thin film materials is an array of nanoparticles. These are arranged with a period which is shorter than the wavelength they are

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**Figure 10.** a) Schematics of the patterned solar cell. b) Snapshot of an imprinted, patterned, solar cell chip. Each colored square is a different area where the pattern has different particle diameter and pitch. c) SEM of Ag-coated patterns (290 nm diameter particles with 500 nm pitch). d) Electrical measurements for a-Si:H with intrinsic layer thickness 160 nm. Reproduced with permission.\cite{93} Copyright 2010, OSA.

**Figure 11.** a) Schematics of a solar cell with a nanovoid indented grating. b,c) Absorption enhancements for different geometries of the nanovoids. d–g) Magnetic field amplitude distribution at points E, F, G, and H, respectively, from (b). Reproduced with permission.\cite{95} Copyright 2010, OSA.
designed to capture. These metallic nanoparticles are placed in such close proximity in order to support propagating modes across the particle chains, thus trapping light. Lin et al. employed energy transfer (ET) between nanoparticles, which is a form of optical waveguiding, to achieve and efficient light absorption. Surface plasmon ET occurs when the localized plasmon resonances of individual metallic particles (see Section 3.2.1) couple to each other. Lin et al. found that, compared to a conventional waveguide, surface plasmon ET provides larger scattering angles, finally yielding, after optimization of the geometry with a genetic algorithm, a relative absorption enhancement of 46.95% for a silicon film of 300 nm.

Very recently, a novel plasmonic architecture, initially envisioned for plasmon management, was proposed for harvesting solar radiation. These plasmon cavities are based on the coupling of plasmon resonances achieved by tailoring metallic films, with optical Fabry–Perot like cavities. Chou and Ding investigated such a structure with the purpose of realizing a solar cell prototype. They fabricated a centimeter-scale device where a hole array in a gold layer was placed on top of an organic ultrathin film (the active layer). The back contact was an Al film, which acted also as reflector for the Fabry–Perot cavity of the plasmon cavity. In contrast with ref. 104, where absorption coming from the spacer between the two metal films is negligible, for this device, the plasmonic properties of the structure had to be engineered to compensate for the absorption occurring in the active layer. The author realized a plasmonic–organic solar cell with a short-circuit current density increase of 41% and a power conversion efficiency enhancement of 52%.

3. Disordered Photonic Structures

3.1. Disordered Dielectric Photonic Structures

One of the first optical mechanisms considered to increment the absorbance performance of active materials for photovoltaics was the random scattering of light, generally achieved by disordered structures. According to the scattering strength of the disordered system, different regimes of light transport are available. For (quasi-)single scattering, the direction of light is randomized, generally with a Lambertian angular distribution, which can be used to increase the light path in the absorbing material. For the case of multiple scattering, light diffusion takes place when the scattering strength is weak. When the scattering strength is so strong enough that interference effects become predominant, the light undergoes subdiffusion.
eventually leading to a complete halt of light transport, the so-called Anderson localization of light.\textsuperscript{108} A (sub-)diffusive process has the clear advantage of slowing down light transport to increase the path length of light inside a material and, thus, the probability for light to be absorbed.

The idea to exploit the interference effects arising from multiple scattering of light to increase its absorption dates back to the eighties.\textsuperscript{109} In this pioneering work, S. John demonstrated that the effect of a small imaginary part of the dielectric constant on the propagation of waves in a disordered medium close to the Anderson transition induces a divergence of the absorption coefficient. This effect is attributed to the extremely slow diffusive propagation of energy in the disordered medium. The transport of light in this class of system is driven by modes characterized by resonances of finite spectral width and spatial extent, generated by the interference between multiple scattered light waves.\textsuperscript{108} Indeed, every scattering event randomizes the direction of propagation and the phase of the electromagnetic wave, yet giving the possibility to define photonic modes with a characteristic spatial profile and lifetime. In diffusive systems, the scattering mean free paths—the distance covered by light between two scattering events—\textsuperscript{108} is much longer than its wavelength \( \lambda \), and the modes spectrally overlap and are spatially delocalized over the sample. When the scattering mean free path, \( l_s \), becomes comparable to the wavelength, the modes are spectrally well separated and spatially isolated, and the propagation of light through the system is inhibited.\textsuperscript{108}

Figure 15a and b schematically depict the spatial distribution of a diffusive mode and a localized mode, respectively. For the sake of clarity, the modes are represented as two-dimensional. However, it has to be pointed out that the Anderson transition occurs only in 3D, whereas in 2D the modes are always localized,\textsuperscript{108} albeit their extension can vary significantly.\textsuperscript{110} In such a subdiffusive system, light performs many oscillations before escaping the sample, thus increasing the probability that it will be absorbed.

3.1.1. Early Designs: Lambertian Scattering

To date, the most practical solutions make use of disordered photonic materials, employing either disordered gratings or rough surfaces. The integration of these surfaces just above or

![Figure 14](https://www.MaterialsViews.com/figure/14)

**Figure 14.** a) Schematic of the plasmonic cavity with a subwavelength hole-array solar cell (PlaCSH). b) SEM of the Au nanostructured film (175 nm diameter and 200 nm pitch hole array). c) Snapshot of 4 inch nanoinprint mold used. d) EQE spectrum of PlaCSH solar cell (SC), ITO-SC, and the absorption length in P3HT:PCBM (85 nm thick on glass). Measured EQE spectrum of PlaCSH and solar cell without nanostructuring of the ITO film; measured absorption spectrum the bare active layer. Reproduced with permission.\textsuperscript{106} Copyright 2013, OSA.

![Figure 15](https://www.advopticalmat.de/figure/15)

**Figure 15.** Intensity profile of a delocalized mode (left), and a localized mode (right). In both cases the modes are composed by collection of speckles. For delocalized modes the envelop of the speckle intensity is almost constant as a function of the position and it depends only on the boundary of the samples. In the localized regime the envelop of the speckle pattern intensity decreases exponentially in all directions.
Figure 16. a) The ability of an antireflection coating (ARC) to maximize optical absorption is limited because the optical path length is not altered. b,c) Incoherent or geometric light-trapping scheme, where random scattering is used to increase the optical path length inside the photoactive region. d) Coherent light-trapping approach where interference, diffraction, and optical electric-field concentration are exploited to enhance the likelihood that an incident photon is absorbed in the photoactive region.

below the active material allows spreading of the incident light, increasing the optical path of each light ray and, therefore, the probability of it being absorbed. Other advantages come from the decrease in the reflection of the incident light, thanks to better refractive index matching between the absorber and the external environment. Moreover, this approach does not directly modify the active material and does not influence its electronic properties, as would happen if the scattering centers were embedded in the active layer. The upper limit for the absorption enhancement that can be achieved using a diffusive mechanism has been calculated by E. Yablonovitch. Within the ray optics approximation, this limit sets the maximum absorption enhancement of a rough surface (in double-pass configuration) with respect to flat (single pass) geometry. As mentioned in Section 2.1, this limit is 4πn², where n is the refractive index of the active layer. For instance, by roughening a slab of silicon and using at the bottom of it a back-reflector, it is theoretically possible to enhance the absorption by a factor of 50, in the visible range. Although this limit does not take into account interference effects, it is often chosen as a reference value for absorption enhancement in photovoltaic materials.

A conceptually simple implementation of photonic disorder for solar cells can be achieved, for example, by smearing the surface of the active material with a disordered arrangement of scatterers, e.g., small dielectric spheres, or more simply by gently roughening its surface. Figure 16 shows schematic representations of solar cells. The simpler architecture is a flat surface (Figure 16a), where a possible antireflection coating is deposited on top. The optical path length is not altered, and absorption is limited by the single or double pass of the photon through the active layer. Only by increasing its thickness it is possible to enhance the absorption efficiency. Figure 16b and c show two possible implementations of how to take advantage of random scattering to enhance the absorption efficiency: In the first case, the presence of disordered dielectric spheres on the top of the active layer is able to spread the light through the active material, while in the second case, similar results are achieved by roughening its surface. Note that the aim here is to scatter enough light so as to have a significant increase of absorption, avoiding, though, the induction of a multiple light scattering process that would reflect most of the impinging light. In most cases, this haze is obtained through texturing of the silicon surfaces or TCO layers. A novel realization of this concept was recently proposed by Fang et al. They developed a new kind of cellulose paper with ultrahigh optical transparency (>90%) and ultrahigh haze (>60%) to be employed as light scattering substrate for photovoltaic devices. When this cellulose system is placed above a silicon wafer, a relative absorption enhancement of 10–18% is measured in the range 400–1000 nm. This material was also able to enhance the power conversion efficiency of an organic solar cell by 10%, by simply being added on its surface.

3.1.2. Coherent Light Trapping in Thin Films through Photonic Disordered Modes

Nowadays, it is well accepted that the most appropriate photonic architectures to be employed in ultrathin film solar cells are designed in planar waveguide configurations. To fully exploit the potential of disordered photonic systems and to benefit from coherent light-trapping mechanisms, the scattering elements have to be embedded into the active material. Figure 16d shows the basic principle of the coherent light-trapping mechanism based on modal coupling. In this case, the wave nature of light is completely exploited, being the thickness of the active layer and the typical pitch of the photonic material comparable with the incident wavelength (see Section 2.1). The amount of coupled and reflected light, the acceptance angles, and the polarization response can be engineered by playing with the size, depth, and positional correlation length of the scattering centers. All these considerations hold for both deterministic and disordered 2D photonic structures, but investigations of the latter for harvesting solar radiation are scarce. 2D architectures show several advantages with respect to 3D arrangements of scattering centers. The most important is that the probability to trap light and create long-living modes is much higher than in three dimensions. Other advantages, common also to periodic structures, are related to the intrinsic 2D nature of the system that allows direct access to quasi-guided modes from the third dimension and to local engineering of the material. Planar architectures are also compatible with standard growing processes, and they can be integrated with electronic components. Coherent light-trapping mechanisms were initially developed in 2D deterministic photonic structures and nowadays...
are often investigated (see Section 2.1). Nevertheless, such an ability generally comes at the cost of a limited set of operating conditions, i.e., a small frequency bandwidth, a narrow acceptance angle range, and a single polarization operation. All these limitations, which can be detrimental for photovoltaic applications, can be overcome by considering 2D disordered modes. As mentioned above, these modes are localized, by virtue of the dimensionality of the system, and intrinsically lossy. Indeed, even considering an absorption-free material, the out-of-plane scattering induced by the in-plane multiple scattering would be non-negligible. Although the in-plane transport is inhibited, the lifetime of disordered modes decreases significantly with respect to deterministic structures, thus incrementing the vertical light-coupling efficiency. These characteristics are also followed by an increase of the acceptance angles and a flattening of the spectral response. The first work to investigate how the nature of these optical modes can be exploited for photovoltaic applications was carried on by Vynck et al. They studied a disordered photonic slab whose architecture is similar to that of Figure 17, i.e., a dielectric membrane perforated with cylindrical air holes acting as scattering centers. Through a detailed analysis of the modes present in the system, they calculated the Fourier resonances $M$ (see Section 2.1) for a large spectral bandwidth, as shown in Figure 17 in normalized units. For low frequencies around $t/\lambda = 0.6$ (t being the film thickness), the resonance distribution exhibits a well-defined peak, corresponding to a propagating mode with an effective refractive index. In this situation, only a few $M$ resonances are present above the light line (see Section 2.1). Increasing the normalized frequency, a progressive broadening of the peak, associated with a stronger light scattering by the holes, is observed, and the $M$-resonances broadly spread over the reciprocal space, leading to an increase of the wavevector density above the light line. As shown in Section 2.1, the amount of wavevectors above the light line are directly related to the coupling efficiency of light inside the dielectric membrane. The almost uniform distribution of the resonances above the light line, in frequency and reciprocal space, indicates that the light-coupling efficiency depends only weakly on the wavelength and angle of incidence. This lead to an increase of the absorption in thin films, which is broadband, omnidirectional, and polarization-insensitive, as experimentally proven by Burresi et al. Vynck et al. also proposed a novel kind of architecture for harvesting solar radiation: By introducing spatial correlations in the disordered distribution of scatterers, they obtained a disordered (nondeterministic) photonic structure with short-range correlations, as shown in the inset of Figure 17d. The effect of these characteristic structural properties can be clearly observed in the photonic dispersions of Figure 17c,d. It is easy to see that the amount of resonances lying above the light line in the presence of spatial correlations depends on the normalized frequency, $t/\lambda$. Indeed, by playing with structural parameters it is possible to engineer and redistribute the amount of leaky resonances, thus enhancing or depleting the probability to couple light inside the dielectric film. The calculated relative absorption enhancement—with respect to the bare slab—of nanopatterned thin a-Si films integrated in the 600–800 nm wavelength range of the solar spectrum is 230%.

Figure 17. a) SEM image of a 2D disordered photonic material on a suspended membrane. b) Schematic representation of the multiple scattering of guided waves. The balance between the amount of guided and radiative number of resonances determine the coupling efficiency from the outside and the lifetime of localized modes. This is calculated in (c) and (d) for a random and a correlated disordered hole pattern, where the dashed line correspond to the light cone. Reproduced with permission. Copyright 2012, Macmillan Publishers Ltd.
for a completely random pattern of scattering centers, and 260% for the correlated case. These values are to be compared with the same quantity in the completely ordered counterpart, that is, 230%. These initial results have driven recent research efforts around disordered nanophotonic materials to enhance absorption efficiency.

Several investigations, both theoretical and experimental, have looked at more realistic geometries for thin-films solar cells. All these investigations showed that disordered photonic nanostructures yield comparable if not superior absorption efficiency with respect to their deterministic counterparts. This is extremely promising for future applications. Given the statistical nature of the optical properties of disordered photonic nanostructures, they are intrinsically more robust towards the structural imperfections arising during the fabrication processes. The displacement of scatterers or the variation in their geometry with respect to the intended pattern would not change the average properties, leaving unaltered the overall performance of the device. This robustness suggests that less accurate, and thus less expensive, fabrication methodologies could be developed for a cost-effective realization of photonic-based solar cells. In this respect, very recently, Paetzold et al. performed an experimental investigation of the role of disorder in photonic light-trapping structures etched in the front TCO layer of a-Si:H solar cells (Figure 18a). The impact of Gaussian stochastic displacement (Figure 18b) of initially periodic arrangements of nanostructures was studied. While at small wavelengths, light is absorbed in the first tenth of a nanometer from the surface, at long wavelengths, strong coupling to specific leaky waveguide modes occurs (Figure 18c). Increasing the displacements of the scatterers leads to broader resonances in the medium, which improves the external quantum efficiency in the bandwidth around 700 nm. For this reason, relative enhancements up to 60% of the short-circuit current Jsc compared to those for periodic structures, are observed (Figure 18d).

In these peculiar disordered structures, a trade-off between the mode lifetime τ (defining the coupling efficiency from the vertical direction) and the absorption time τa (the average time after which light is absorbed by the dielectric medium) is crucial to properly engineer the structure. When τ is too large, light will not couple to the disordered modes. When τ is too short with respect to τa, light coupled to the modes will escape before being absorbed. How these two lifetimes relate to the in-plane transport properties is currently under investigation.

3.2. Disordered Plasmonic Structures

Metals do not only sustain surface (see Section 2.2) but also volume charge density oscillations. This is the case for small metal particles, that is, particles whose size is comparable to the penetration depth of the electromagnetic waves. At optical frequencies, such a penetration depth is around 10 nm and, thus, for particles of a few hundreds of nanometers (smaller than the excitation wavelength), the optical response of the nanoparticle is dielectric-like. Given the very high complex-valued dielectric constant of metals, a series of spectral resonances in the scattering and absorption cross-section arises: so-called localized surface plasmon resonances (LSPRs). As a result, these wavelength-dependent cross-sections can be several times the cross-sectional area of the particle. The extinction, scattering, and absorption efficiency, defined as the ratio between the corresponding cross-sections and the cross-sectional area, can be exactly calculated for spherical nanoparticles of radius R by Mie theory as

\[
Q = \frac{2}{\pi} \sum (2l + 1) \Re(a_l + ib_l) \tag{4}
\]

\[
Q = \frac{2}{\pi} \sum (2l + 1) \{a_l + (ib_l)\} \tag{5}
\]

\[
Q = Q_s + Q_a \tag{6}
\]

\[
h = \frac{n_2 \psi_l(y) \eta_l(x) - n_1 \psi_l(y) \eta_l(x)}{n_1 \psi_l(y) \eta_l(x) - n_2 \psi_l(y) \eta_l(x)} \tag{7}
\]

\[
a = \frac{n_2 \psi_l(y) \eta_l(x) - n_1 \psi_l(y) \eta_l(x)}{n_1 \psi_l(y) \eta_l(x) - n_2 \psi_l(y) \eta_l(x)} \tag{8}
\]

Here, ψl and ηl are the Riccati–Bessel functions of the first and third kind, x = n_1 k R and y = n_2 k R are normalized parameters, n_1 and n_2 are the complex-valued refractive indexes of the sphere and environment, respectively, and k is the wavevector of light. Depending on the relation between λ and R, i.e., on the normalized parameters x and y, several resonances appear in Q and Q_a, which are associated with different multipole moments of the particle (dipole, quadrupole, octupole moments, both electric and magnetic). Figure 19 shows the scattering and absorption coefficients for silver and aluminium nanoparticles in a polymeric environment (refractive index 1.5) for different radii. The dielectric constants as a function of frequency of these materials have been taken from the literature. Clearly, by properly choosing the material and the dimension of the nanoparticle, it is possible to tune the resonances so as to cover the entire visible spectrum, a property extremely useful for solar applications, as we will now show.

One of the most striking properties of LSPRs is the capability to concentrate the optical field close to the particle surface. For the case of SPPs (Section 2.2), this is due to the accumulation of free electrons which oscillate following the direction of the driving electric field. As a result, since the field is higher where the charges accumulate the most, the location of the field enhancement is determined by the light polarization and the shape of the particle. In case of an isotropic particle, only the polarization will determine the field distribution (Figure 20a). In the case of particular geometries, the field tends to accumulate where the radius of curvature is minimum, similar to the lightning-rod effect at low frequencies (Figure 20b). At optical frequencies, however, the presence of LSPRs increments the field enhancement much more with respect to the lightning-rod effect. In this regard, metal nanoparticles can be considered optical antennas, which improve the light–matter interactions.
interaction through near-field coupling. Systems composed of nanoparticles of various geometries have been investigated in order to enhance more effectively the local field. This phenomenon was used in a variety of applications, ranging from surface-enhanced Raman scattering \cite{151,152} to sensing,\cite{153} to nonlinear optics\cite{154,155} and photovoltaics.

As a final remark, it should be noted that the realization of plasmonic nanoparticles with different shapes and types of aggregates are often obtained with self-assembly fabrication techniques.\cite{156} In general, photonic architectures designed to improve the absorption of ultrathin solar cells that can be fabricated by self-assembly techniques are particularly welcomed by industry, given their low-cost implementation. Self assembly, if not specifically controlled, naturally leads to the realization of disordered structures.

3.2.1. Plasmonic Nanoparticles and Photovoltaics

Given their large scattering efficiency, plasmon nanoparticles can be used to efficiently couple light into the absorbing thin films.\cite{157–159} One of the first attempts to use metal nanoparticles on top of an a-Si solar cell was carried out by Derkacs et al.,\cite{157} who found an 8% increase in short-circuit current density. In general, this strategy turns out to be particularly suited to relatively thick films with a high refractive index.\cite{158,160,161} When a nanoparticle is placed at the interface between two dielectric materials, most of the scattered light couples to the high-refractive-index medium.\cite{158} Figure 20c shows the fraction of scattered light in an absorbing film as a function of the shape of the particles at the film interface. By tuning the size and material, the resonant scattering cross-section of the nanoparticles can be employed to increase the absorption of a portion of the solar spectrum. This can lead to the realization of thin films which, for instance, absorb in the UV but are semitransparent in the visible and NIR regions.\cite{162}

The use of nanoparticles to increase light harvesting must deal with their ever-present absorption, which can become extremely pronounced for particles of a few tens of nanometers (see Figure 19). Very recently, scientists have been trying to exploit this absorption by collecting the optically generated hot carriers of the metal itself.\cite{163–165} These hot carriers are injected into the conduction bands of materials in close proximity with the particles. Shao et al. deposited gold nanoparticles on a TiO\textsubscript{2} nanotube array (Figure 21).
and carried out photocurrent experiments. They found an enhancement of current (145%) when illuminating the sample with respect to the current measured in darkness, which is attributed to the hot carriers injected into the TiO₂.

An interesting alternative approach for harvesting solar radiation employing plasmonic nanoparticles was recently implemented by Fahim et al. The authors succeeded in preparing a layer of random gold nanoparticles embedded in SiNₓ to use as an antireflection coating on top of a c-Si solar cell. The work presented a study of the photocurrent enhancement as a function of the distance between the plasmonic nanoparticles and the c-Si substrate (see Figure 22). At 100 nm, the photocurrent enhancement was minute and mostly due to the strong scattering of the gold nanoparticles, which increased the light path. As the distance between c-Si interface and the plasmonic nanoparticles was enlarged, the photocurrent enhancement increased significantly, up to an overall 6% augmentation for a distance of 10 nm. This effect was attributed to the large field enhancement close to the nanoparticle surface, which concentrates the light intensity and thus increases the optical absorption.

3.2.2. Complex Local Surface Plasmon Architectures

The optical response of nanoparticles has been thoroughly investigated, and new shapes, designs, and functionalizations have been envisioned, mostly with the intent to increase the concentration of the field or the scattering efficiency while keeping the plasmon absorption as low as possible. One of the first ideas to improve the plasmon–matter interaction, not only for photovoltaics but also for sensing and other applications, is the use of dimers of nanoparticles. One of the first ideas to improve the plasmon–matter interaction, not only for photovoltaics but also for sensing and other applications, is the use of dimers of nanoparticles.

As these nanoparticles can be considered optical nanoantennas, the attention of scientists has focused on their optical response as a function of their shape, such as rods, stars, prisms, and triangles, in order to spectrally tune and manipulate the absorption and field enhancement. Tailoring the shape of metallic nanoparticles allows control over their spectral response, which can be tuned to increase the weak absorption of active materials in a certain spectral region, generally in the NIR. One of the most interesting solutions is the use of plasmon nanoshells. These are made of dielectric particles coated with a very thin layer of metal, usually gold or silver. Such particles have plasmon resonances very sensitive to the relative size of their core and shell layers. This sensitivity arises from the so-called hybridization between the plasmons of the inner and outer metallic interfaces.

The resonance frequencies of nanoshells can be extended from the visible to the NIR domain. Very recently, Paz-Soldan et al. realized a quantum dot solar cell in which a plasmon nanoshell (Figure 23) was integrated. This architecture yields a scattering cross-section much higher than that...
The current density enhancement is about 13%. Reproduced with permission. Copyright 2012, AIP Publishing LLC.

Figure 22. Schematic representation of a crystalline silicon solar cell where gold nanoparticles are embedded within a silicon nitride layer. b) Current density enhancement as a function of spacing layer thickness obtained with gold nanoparticles 60 nm in diameter. Reproduced with permission.[166] Copyright 2012, AIP Publishing LLC.

of standard particles, whereas the absorption cross-section is comparable with the latter. Exploiting the large field enhancement at the metal interface, the active layer of quantum dots increases light absorption in the NIR domain, yielding an overall 35% enhancement in photocurrent.

4. Conclusions
In this review, we have discussed the state-of-the-art of micro- and nanophotonics for photovoltaic applications. We focused our attention on the optical performances of the specific designs of photonic and plasmonic structures that can be used to maximize the absorption of the incident light, made with deterministic or disordered architectures. Although it is well known that these structures can enhance significantly the absorption of dielectric films, even for extremely thin films, only recently has the impact of photonic architectures on the actual current production been tested. Nowadays, the first prototypes based on ray optics mechanisms, light trapping, modal coupling approaches, and even plasmonic principles have been fabricated. In all these cases it is possible to take advantage of deterministic and disordered photonic/plasmonic designs.

Dielectric structures engineered on length scales longer than the incident optical wavelengths work in the ray optical regime and are suited for relatively thick solar cells. This class of structure allows one to decrease the amount of reflected light by texturing the front surface of the film, avoiding possible damage to the active material and thus preventing the creation of recombination centers for the free carrier.

The introduction of thin-film solar cells allows a reduction of the amount of raw materials, hence reducing costs and also minimizing the path length that the photogenerated carriers have to cover to reach the contacts. Ideally, the thickness should be reduced even further in order to also capture so-called hot electrons, whose diffusion length is extremely short. However, such a minute thickness prevents the absorption of optical energies close to the edge of the electronic bandgap of the active material. In this range of energy, the absorption length of light is much longer than the thickness of the film and, consequently, the radiation is not absorbed. Ray optics approaches are not sufficient to significantly improve the absorption of such thin films, and nanophotonic methodologies which fully exploit the wave nature of light have to be employed. Light-trapping architectures, spanning from deterministic to disordered, are designed to couple and store light inside the active layer. Alternatively, the extraordinary field enhancement of surface plasmon polaritons in close proximity of the active layer can be exploited to increase the light absorption. However, to induce a significant absorption enhancement, the active material should be directly engineered with nanopatterning.

Generally, this leads to a decrease in the electronic performance by creating electronic surface defects between the bulk and the surfaces of the scattering elements, thus increasing unwanted recombination mechanisms. We show in this review that important progress in this respect has been made by the scientific community which will pave the way for future industrial applications.

The main contribution to the Shockley–Queisser limit for the efficiency of a single-junction solar cell comes from the thermalization of hot carriers and the absorption bandwidth of the cell active material. The most efficient solutions that allow one to overcome these problems are multi-junction and quantum-dot-based solar cells, which exhibit efficiencies beyond 40%. Nevertheless, these architectures are very expensive in terms of production processes and the cost of raw materials, and thus are not suitable on an industrial scale. All these issues cannot be overcome by simply increasing the light absorption, which accounts for a small percentage of the enhancement in terms of energy conversion. Hence, the nanophotonic photovoltaics community aims to drastically modify the standard architecture of solar cells. Light-trapping schemes, together with plasmonic effects, have to be integrated in order to gain the best from each approach. The

Figure 23. a) Schematic of a quantum dot heterojunction device with embedded gold nanoshells. b) Top-view SEM showing the nanoshells after preparation (scale bar 1 µm). c) TEM showing a cross-sectional image of single gold nanoshells embedded in a quantum dot film (scale bar 100 nm). d) Measured J–V characteristics under irradiation with a solar simulator. The current density enhancement is about 13%. Reproduced with permission.[177] Copyright 2013, the Amercan Chemical Society.
Schockley–Queisser limit depends on the radiation intensity and, thus, by increasing its concentration with nanophotonic methodologies, would raise the efficiency limit. Extremely thin films engineered by nanophotonic principles can be used to realize solar cells in which the distance covered by the carriers to reach the contacts is reduced. For example, radial p–n junction Si nanowires have been successfully realized, in which the photogenerated carriers only need to cross the nanowire transversal size in order to be collected.\(^{[177]}\) In this respect, inspiration can come from organic photovoltaic devices and dye-sensitized solar cells, where the n-type and the p-type materials are morphologically mixed, making the interaction between electrons and holes less probable. Another possible scenario is offered by quantum dot solar cells that can be realized at room temperature from colloidal solutions.\(^{[179,180]}\) The advantage of semiconductor nanocrystals is to have an electronic bandgap that depends on the dot size, increasing the bandgap by more than 1 eV compared with the bulk value. This allows us to properly engineer the width of the electronic bandgap, making possible the use of unconventional materials as active materials for solar cells.

The road that researchers have to follow towards novel solar cells made compatible with industrial-scale requirements is still long, and only by merging different solutions will it be possible to get closer to the Schockley–Queisser limit and beyond that, by taking advantage of innovative trapping schemes and electronic bandgap engineering.

5. Glossary

Absorption Enhancement: This is defined as \( AE = A_{ph} / A \), where \( A_{ph} \) is the absorption of a nanophotonic solar cell and \( A \) the absorption of bare solar cell.

Anderson Localization of Light: This phenomenon, occurring when light experiences an extremely strong multiple scattering, leads to a complete halt of light transport in disordered systems.

Diffraction Limit: Theoretical maximum resolution of an optical microscope which, according to Abbe’s calculations, is \( d = \lambda / NA \), where \( \lambda \) is the wavelength of light and \( NA \) is the numerical aperture of the optical system employed.

Diffusion: A phenomenon occurring when light propagates through a system and undergoes multiple scattering events. Generally it is described by the diffusion equation.

External Quantum Efficiency: The ratio between the number of photogenerated electrons and the number of photons incident on the solar cell.

Fill Factor: The ratio between the product \( J_{sc} \times V_{oc} \) and the actual maximum obtainable power \( P_{max} \).

Guided Modes: A waveguide mode is a spatial distribution of optical energy that is confined within the waveguide by total internal reflection.

Hot Electrons: Electrons with energy significantly above the electronic bandgap, generally generated with the absorption of blue light.

Internal Quantum Efficiency: The ratio between the number of absorbed photons and the number of photogenerated electrons.

Lambertian Scattering: Lambert’s cosine law says that the intensity of the diffusively reflected light from a rough surface is proportional to the cosine of the angle between the normal axis to the surface and the direction of observation.

Open-Circuit Voltage: Defined as the voltage \( V_{oc} \) at the cell terminals when the current is zero.

p–n junction: A boundary interface between two semiconductors with different doping types.

Power Conversion Efficiency: Efficiency of a solar cell defined as \( \eta = \left( \frac{ff \times J_{sc} \times V_{oc}}{P_{inc}} \right) \), where \( ff \) is the fill factor, \( J_{sc} \) the short-circuit current density, \( V_{oc} \) the open-circuit voltage and \( P_{inc} \) the incident power density.

Relative Absorption Enhancement: Defined as \( AE = A_{ph} / A \).

Scattering Mean Free Path: Average distance between scattering events in a system where light undergoes multiple scattering events.

Schockley–Queisser Limit: Maximum theoretical power conversion efficiency (33.7%) for a single p–n junction solar cell.

Schottky Junction: A boundary interface between a semiconductor and a metal.

Short-Circuit Current Density: Defined as the density of the current \( J_{sc} \) when the voltage at the cell terminals is zero.

Structure Factor: A mathematical tool commonly used in crystallography that describes how a material scattering incident radiation.

Subdiffusion: A phenomenon that can occur when light propagates through a system and undergoes multiple scattering events due to the presence of strong scattering. The spreading of light is slower than in the diffusive regime, and it cannot be described by the standard diffusion equation.

Total Internal Reflection: When light is incident upon a dielectric surface above a certain critical angle it undergoes complete reflection.

Transparent Conductive Oxide: A semitransparent conductive layer that works as an ohmic contact, most commonly in the form of indium tin oxide (ITO).

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