

Progress and Design Concerns of Nanostructured Solar Energy Harvesting Devices

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Integrating devices with nanostructures is considered a promising strategy to improve the performance of solar energy harvesting devices such as photovoltaic (PV) devices and photoelectrochemical (PEC) solar water splitting devices. Extensive efforts have been exerted to improve the power conversion efficiencies (PCE) of such devices by utilizing novel nanostructures to revolutionize device structural designs. The thicknesses of light absorber and material consumption can be substantially reduced because of light trapping with nanostructures. Meanwhile, the utilization of nanostructures can also result in more effective carrier collection by shortening the photogenerated carrier collection path length. Nevertheless, performance optimization of nanostructured solar energy harvesting devices requires a rational design of various aspects of the nanostructures, such as their shape, aspect ratio, periodicity, etc. Without this, the utilization of nanostructures can lead to compromised device performance as the incorporation of these structures can result in defects and additional carrier recombination. The design guidelines of solar energy harvesting devices are summarized, including thin film non-uniformity on nanostructures, surface recombination, parasitic absorption, and the importance of uniform distribution of photo-generated carriers. A systematic view of the design concerns will assist better understanding of device physics and benefit the fabrication of high performance devices in the future.



1. Introduction

Efficient light harvesting is of crucial importance for high performance solar energy harvesting devices including photovoltaic (PV) devices and photo-electrochemical (PEC) solar water splitting devices. In past decades, extensive studies on material and device design innovation have been performed to improve the power conversion efficiencies (PCEs) of such devices. For example, light management schemes such as antireflection coatings, back-reflectors, and surface texturing were explored in order to reduce the optical losses from the devices.^[1-11] In particular, the utilization of nanostructures is considered a promising approach to improve the optical absorption as well as the PCE of solar energy harvesting devices. With regard to this, various nanostructures including nanospike (NSP), nanowire (NW)/ nanopillar (NPL) and nanocone (NC) have been explored, and they have demonstrated promising potency to improve the optical absorption and PCE of solar energy harvesting devices as opposed to their planar counterpart.^[12-32] In addition, it was found that the thicknesses of light absorber and material consumption can be significantly reduced because of the improved light trapping. Therefore, nanostructures can not only improve optical absorption, but also simultaneously shorten the photo-generated carrier collection length and result in more effective carrier collection.^[33-36] Radial p-n junctions and nanostructured electrodes, in particular, have been proven effective for the aforementioned purposes. Nonetheless, much literature has reported that the proper design of solar energy harvesting devices is of utmost importance and optimizations of different key aspects are needed. On one hand, the utilization of nanostructures can improve device performance via more effective light trapping. On the other hand, it may increase the complexity of device fabrication. For example, conformal coating of PV thin films on nanostructures is more challenging as compared to that on planar substrates due to the increased surface roughness. In some cases, this can have a detrimental effect on device performance.^[37-39] Moreover, the utilization of nanostructures will unavoidably increase the surface area, and thus an increase of surface recombination has to be considered when designing high performance solar energy harvesting devices. It is worth mentioning that an increase of surface recombination will particularly affect the performance of devices based on active materials with high surface recombination velocity such as single crystalline silicon, GaAs, etc.^[34,40-42] Furthermore, while nanostructures can increase the overall optical absorption of solar energy harvesting devices, it is important to evaluate how much light absorption enhancement is contributed by the active material as opposed to the passive materials in the device, such as electrodes, since only photocarriers generated in the active light absorber can contribute to the photo-current. Parasitic absorption occurring in the electrodes can cancel out the optical absorption enhancement introduced by nanostructure photon management.^[16,43] In addition to the above mentioned points, photo-carrier distribution is another factor to be considered when designing nanostructured solar energy harvesting devices, especially for PEC solar water splitting devices.^[44–46] In this review, we will



firstly summarize the progress of nanostructured solar energy harvesting devices with emphasis on introducing various nanotexturization strategies. Thereafter, we will discuss the key aspects when designing highly efficient nanostructured solar energy harvesting devices, including PV thin films nonuniformity on nanostructures, surface recombination, parasitic absorption and the importance of uniform distribution of photo-generated carriers.

2. Brief Review of Light Harvesting with Nanostructures

Over the past decades, many different types of nanostructures, such as nanowires/nanopillars, nanospikes and nanocones.^[4,5,19,25,27,28,31,47-70] have been employed to achieve a rational light management design for solar energy harvesting devices. Various nanotexturization approaches were explored and can be categorized in general as top-down approaches bottom-up approaches, and a combination of them. Among these approaches, the top-down method has the highest degree of controllability of the nanostructure geometries such as ordering and aspect ratio. In one example, Jeong et al. reported an ultrathin nanocone single crystalline silicon PV device with only a 10 µm absorber fabricated by colloidal lithography and dry-etching. Such a PV device with a nanocone light trapping structure and all-back contact design could achieve a PCE of 13.7%.^[47] Notably, the external quantum efficiency (EQE) at 400 nm wavelength was 80%, which was 15% higher than that of other nanostructured Si solar cells and 200% higher than that of III-V nanowire solar cells.^[41,43] The solar cell could effectively perform light trapping using front-side nanocones with a height of only about 400 nm and total absorber thickness of only 10 µm. It resulted in a short-circuit current density (J $_{\rm sc})$ of 29.0 mA cm $^{-2}$ which is 30.7% higher than that on a planar silicon solar cell coated with Si₃N₄ as an anti-reflection layer. Furthermore, Wang et al. reported a double-sided grating design of an ultrathin-film silicon solar cell and the optimized cell design yielded a photocurrent of 34.6 mAcm⁻² at an equivalent absorber thickness of 2 µm, which is close to the Yablonovitch limit.^[2,28] Displayed in

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Figure 1a is a schematic of one of the ultra-thin silicon films with nanocone structures studied in this work. The optical absorption spectrum of a specific nanocone structure was calculated by rigorous coupled wave analysis (RCWA).^[71-73] From the calculated absorption spectra, J_{sc} was determined by assuming air mass 1.5 (AM 1.5) solar spectrum irradiance. Plots shown in Figure 1b are the calculated photocurrent of the ultra-thin silicon film with (a) double-sided grating, (b) top-only grating, (c) bottom-only grating and (d) un-patterned film. As clearly shown in the plot, the photocurrents from the optimized double-sided grating structures are very close to the theoretical Yablonovitch limit and superior to other structures. More importantly, the optimized structure generated a J_{sc} of 34.6 mAcm⁻² with only 2 µm equivalent absorber thickness. In addition, Mariani et al. have reported a direct-bandgap core-multi-shell GaAs NPL array solar cell fabricated by photolithography and selective area MOCVD which achieved a PCE of 7.43%.^[57] Intriguingly, dome-shaped indium-doped Tin oxide was formed by sputtering, which functioned as a subwavelength nanolens to intensify the optical field within the NPL absorber. As opposed to the top-down method, bottom-up fabrication of nanostructures is an enticing approach to fabricate nanostructures without using costly processes such as lithography and drv-etching.^[5,17,22,32,51,63,64,74-77] As an example, Fan et al. reported ordered arrays of Germanium (Ge) dual-diameter Nanopillars (DNPLs) with different diameters at the tip and base fabricated inside self-organized anodic aluminum oxide (AAO) templates. Such DNPLs presented an impressive absorption of 99% of the incident light over a wavelength ranging from 300 to 900 nm with a thickness of only 2 μ m.^[63] Figure 1c shows the scanning electron microscope (SEM) image of a dual-diameter template for VLS growth of Ge and the inset shows the highly ordered as-grown Ge DNPLs with a tip diameter (D1) of ≈ 60 nm and base diameter (D2) of ≈130 nm. In addition, single diameter Ge NPL arrays with a diameter of 60 nm and 130 nm were also fabricated and their measured absorption spectra are displayed in Figure 1d. Evidently, the Ge DNPL array has a 95%-100% optical absorption at wavelength range of 300-900 nm, which is significantly higher and exhibited a broader band of absorption enhancement as compared to the single diameter NPL counterparts. These results demonstrated the design guidelines on the geometries, including height and diameter, of NPLs that can maximize the optical absorption of solar energy harvesting devices. In addition to this, fabrication that combines both top-down and bottom-up approaches was also reported for nanotexturization. In particular, Leung et al. demonstrated nanoimprint assisted anodization which resulted in perfectly ordered AAO nanowell (NWL). Such nanowell performed an impressive optical absorption of 99.2% with only 50 nm of amorphous silicon (a-Si:H) thin film. In addition, optical simulation studies revealed that the geometries of the nanostructure, such as periodicity, can largely facilitate photon capturing of absorber materials.^[12] Other than light trapping under normal incident light, PV devices with omnidirectional light trapping capability are of great interest since the sunlight incident angle varies throughout a day. Therefore, it is crucial for PV devices to maintain





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light harvesting efficiency at an oblique angle of incidence. Accordingly, Lin et al. presented a-Si:H PV devices fabricated on the inverted nanocone (i-cone) substrates and demonstrated enhanced omnidirectional light trapping capability as well as device performance over the flat control device.^[20] In this work, PV devices were fabricated on i-cones with various aspect ratios, which is defined as the ratio of the cone depth over pitch. To investigate the influences of i-cone geometries on device performance, PV devices based on an i-cone with an aspect ratio of 0.25, 0.5, and 1 were fabricated. Figure 1e1 and 1e2 display the cross-sectional SEM image and the modeled cross-sectional electric field intensity (IEI²) distribution of the electromagnetic (EM) wave at 500 nm wavelength of an a-Si:H device fabricated on an i-cone with an aspect ratio of 0.5. The electrical performance of the





Figure 1. a) Schematic diagram of ultra-thin film double-sided silicon nanocone. b) Calculated photocurrent of ultra-thin silicon film with a) doublesided grating, b) top-only grating, c) bottom-only grating, and d) un-patterned film. The black curve represents the Yablonovitch limit.^[28] c) Crosssectional SEM images of an AAO with dual-diameter pore array, and, inset, the Ge DNPLs array after VLS growth. d) Optical characterization of Ge DNPLs array and single diameter NPLs array with diameter of 60 nm and 130 nm.^[63] e) Cross-sectional SEM image and cross-sectional electric field intensity ($|E|^2$) distribution of electromagnetic (EM) wave at 500 nm wavelength of a-Si:H device fabricated on i-cone with aspect ratio of 0.5. f) J-V characteristics of a-Si:H devices based on 1.5 µm pitch i-cone substrates with different aspect ratios and the flat control.^[20] Reproduced with permission.^[28] Copyright 2012, American Chemical Society. Reproduced with permission.^[63] Copyright 2010, American Chemical Society. Reproduced with permission.^[20] Copyright 2014, American Chemical Society.

aforementioned devices were characterized under Air-mass 1.5 global (AM 1.5G) condition and their current densityvoltage characteristic (J-V) are shown in Figure 1f. With a J_{sc} of 15.44 mAcm⁻², open-circuit voltage (V_{oc}) of 0.792 V and fill factor (FF) of 62%, the a-Si:H device fabricated on an i-cone with an aspect ratio of 0.5 outperformed other candidates, which can be attributed to the effective light trapping of the i-cone nanostructure. What is more, the i-cone nano-structure can improve the light harvesting omnidirectionally, which is of paramount significance for the practical deployment of a solar panel without a costly solar tracking system.

3. Benefits from Device Structure Innovation

Since efficient light trapping and effective photo-carrier collection are both essential for high performance solar energy harvesting devices, it is important to take both aspects into

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Figure 2. a) Schematics of radial *p-n* junction architecture that can shorten minority carrier collection length and achieve more effective photocarrier collection. b) SEM image of partially exposed CdS NPL array fabricated in AAO pore array. c) Plot of PCE of CdTe/CdS radial junction PV devices as a function of embedded CdS NPL height (H).^[33] d) Schematic of the cross-section of a nanostructured CQD solar cell. e) Integrated absorption spectra in the PbS CQD films of equal collection distance planar, equal volume planar, and nanostructured device. f) J-V characteristics of planar nano and structured solar cells measured under simulated AM 1.5 illumination.^[35] Reproduced with permission.^[33] Copyright 2009, Nature Publishing Group. Reproduced with permission.^[35] Copyright 2013, Nature Publishing Group.

consideration in order to improve overall power conversion efficiency. In recent years, various approaches have been explored to shorten the photo-carrier collection length and improve carrier collection. In particular, a radial p-n junction was proven to be highly promising to facilitate carrier collection by collecting photo-carriers radially and resulted in a shorter photo-carrier collection path. PV devices with a radial *p-n* junction can allow the use of low-quality materials while maintaining a relatively high PCE, which is favorable for low-cost photovoltaics. As an example, Fan et al. reported a radial junction-based PV device which consisted of highly ordered single crystalline n-type NPL arrays embedded in a polycrystalline p-type CdTe thin film.^[33] As shown in the schematics in Figure 2a, radial junction architecture can provide a shortened minority carrier collection path thus achieving more effective carrier collection. It is worth noting that a CdS/CdTe system has a relatively low surface recombination velocity of 10^3-10^4 cm·s⁻¹ which can alleviate the negative impact by increased surface recombination associated with the high surface/junction area in a NPL radial junction.^[33,78] Figure 2c is the plot of the PCE of the aforementioned CdTe/CdS radial junction PV devices as a function of embedded CdS NPL height (H). It can be seen that the PCE increases from $\approx 0.4\%$ for H = 0 nm to $\approx 6\%$ for H = ≈ 640 nm. In the case of H = 0 nm, the CdS/CdTe junction is only formed at the top surface of the CdS NPLs which results in a low PCE. However, with an increased embedded CdS NPL height, the PCE increases drastically which is ascribed to effective photo-carrier collection of the radial CdS/CdTe junction. These results clearly demonstrate the advantages of utilizing a radial p-n junction design to facilitate photocarrier collection and improve PV performance. On the other hand, as mentioned in the previous section, since nanostructures can largely improve the optical absorption in absorber materials of a PV device, a thinner absorber can be used to absorb the equivalent amount of light as compared to planar substrate. As a result, the photo-carrier collection length can be shortened in a nanostructured PV device, which implies more effective carrier collection. In this regard, nanostructured electrodes can relax the competition between optical absorption and carrier collection of PV devices. In fact, many other types of nanostructured electrodes have also been explored, including nanocones, nanodents and nanospikes, and significant improvements on PV device performance have been demonstrated.^[16,20,37,38,70] Adachi et al. presented a novel back-illuminated type colloidal quantum dot (CQD) PV device and a nanostructured glass electrode was utilized to improve the optical absorption and photo-carrier collection efficiency simultaneously.^[35] Figure 2d shows the schematic of the nanostructured CQD solar cell and the solar cell device was fabricated by depositing PbS CQDs on TiO₂ and ITO coated nanostructured glass substrate followed by MoO₃



and gold electrode deposition. As compared with planar devices made of the equivalent volume of CQDs and with the same photo-carrier collection distance, nanostructured COD PV devices have significantly higher optical absorption, which is presented in Figure 2e. This result suggests that nanostructured electrodes can maximize the optical absorption of PV devices while maintaining a short photo-carrier collection length. J-V characteristics of the planar and nanostructured COD PV devices are shown in Figure 2f and the inset shows the cross-sectional SEM image of nanostructured CQD PV devices. With a J_{sc} of 20.2 mAcm⁻², V_{oc} of 0.57 V and FF of 0.526, the nanostructured CQD PV device yielded a PCE of 6.0%, which outperformed the planar counterpart by 31%. Overall, the above works demonstrate that the proper structural design can greatly improve the photo-carrier collection and performance of solar energy harvesting devices. In the following sections we will review and summarize more specific design rules for high performance devices. In addition, nanotexturization of photoanode of PEC water splitting device can also improve the optical absorption and performance of the devices. For example, Qiu et al. has reported a PEC water splitting device based on an engineered design of a nanospike (NSP) template. With an ultrathin hematite thin film of only 85 nm, NSP can remarkably improve the efficiencies of water splitting as compared to the flat control device due to the enhanced light trapping.^[46] Moreover, Oh et al. has presented a nanostructured black silicon photoanode that can dramatically improves the hydrogen production by providing near-ideal anti-reflection that enables the absorption of most incident light and its conversion to photogenerated electrons and extremely high surface area in direct contact with water that reduces the overpotential needed for the hydrogen half-reaction.^[79] The similar approach were also utilized by Lee et al. and they had reported InP nanopillar photocathodes which can drastically suppress the specular reflectance in wavelength range of 300-900 nm as compared with the planar InP wafer and led to more efficient hydrogen production.^[75]

4. Design Rules for High Performance Solar Energy Harvesting Devices

4.1. Influences of Nanostructures on Carrier Dynamics and Electrical Properties of Active Materials

Apparently, introducing nanostructures for advanced light management can improve the light trapping capability of solar energy harvesting devices. However, in some cases, the electrical properties of active materials and carrier dynamics in devices would be adversely affected leading to degraded device performances. Device physics simulation is a helpful approach to study the effect of solar cell geometries on their efficiencies by systematically tuning the cell geometries and electrical properties of the active material. Kayes et al. revealed the design constraint of a nanorod radial p-n junction solar cell by analyzing a device physics simulation model. In the device physics analysis, electrical parameters of both planar and nanorod solar cell, including power conversion

efficiency, open-circuit voltage and short-circuit current density, were simulated under different geometries and electrical parameters of active materials, such as depletion region trap density and minority carrier diffusion length (L_n). Firstly, the simulation of short-circuit current density J_{sc} versus cell thickness L and minority-electron diffusion length L_n of a nanorod Si solar cell was carried out by assuming the L_n equals the radius (R) of the nanorod in order to eliminate the effect of minority carrier diffusion length. It was found that J_{sc} increased monotonically with the increasing cell thickness L, and L_n has only a minor effect on J_{sc} provided that L_n was set equal to the nanorod radius R. This result was anticipated as more absorption can be achieved by a solar cell with a thicker nanorod. Thereafter, more simulations were completed to investigate the effect of cell thickness on the V_{oc} of planar and nanorod solar cells. Shown in Figure 3a is the 3-D contour plot of Voc versus cell thickness and minority-electron diffusion length. It can be seen that V_{oc} is independent of cell thickness in the planar device and V_{oc} decreases slowly with the increase of the depletion region trap density. The plot in Figure 3b shows the relationship between V_{oc} and cell thickness in the case of the nanorod radial p-n junction. Interestingly, it is found that V_{oc} decreases as the cell thickness increases and it decreases rapidly with the increase of the depleted region trap density. This intriguing result can be attributed to the increase pn junction area due to the nanorod structure and the more recombination that occurred. It is worth pointing out that introducing nanostructures to solar cell devices could lead to a high trap density of active materials and the related studies were reported in other literatures.^[38] Other than nanotexturizing the active materials itself, another common approach is to utilize nanostructure scaffold underneath to the active materials to achieve geometrical light trapping, which was widely adopted in thin-film photovoltaics. On the downside, thin film materials deposited on such a nanostructure scaffold can suffer from localized geometry-induced defects which can be especially severe on high aspect-ratio nanostructures. Hsu et al. reported a-Si:H thin film PV device with nanostructured back reflectors, and investigated the influences of nanostructure morphologies on the optical and electrical performance of devices. In this work, the researchers revealed that nanostructured back reflectors such as convex nanodomes (Figure 3c) can lead to deterioration of the Voc and FF of PV devices, although they provided excellent J_{sc} by efficient light trapping.^[38] As compared with the planar control, PV devices with nanodomes have a substantially lower V_{oc} and FF. The reasons for the lower V_{oc} and FF in nanodome devices can be understood by characterizing the device cross-section with a SEM, which is shown in Figure 3d. While non-uniformity of PV thin film deposition is not the major problem for nanodomes, which is considered to be a low aspect ratio among nanostructures reported in literature.^[49,80–82] the presence of voids became apparent and it was proven detrimental to the device performance. The formation of voids can be explained by the following. During deposition of a-Si:H thin film by plasmaenhanced chemical vapor deposition (PECVD), a region of low-density and porous material circled in Figure 3d was formed in the V-shaped valleys when silicon film was growing





Figure 3. Open-circuit voltage V_{oc} vs cell thickness L of a) planar, and b) radial *p-n* junction nanorod silicon cell.^[34] c) Schematic, and d) SEM image of cross-section of a nanodome a-Si:H solar cell.^[49] e) Cross-sectional SEM image of an NSP-based thin film solar cell with NSP height of around 1200 nm. f) Simulated J-V characteristics of PV devices with three different a-Si:H thicknesses at the sidewall of the NSP^[37] Reproduced with permission.^[34] Copyright 2005, American Institute of Physics. Reproduced with permission.^[49] Copyright 2012, WILEY-VCH. Reproduced with permission.^[37] Copyright 2014, Nature Publishing Group.

and colliding on neighboring nanodomes. In those regions, extra recombination would occur and cause the reduction of V_{oc} and FF, which is also reported in other literature.^[49,81,83] Besides the investigation by experiment, the influences of nanostructure geometries on the electrical properties of active material were also studied by theoretical simulation. Deceglie et al. described a simulation-based approach to study the trade-offs between the light trapping effect by high aspect-ratio nanostructures and the electrical properties of active materials.^[84] In this work, multi-dimensional optical and electrical simulations were coupled to study localized regions of degraded material quality that are induced by light trapping structures in a-Si:H solar cells. On the other hand, in order to fabricate a highly efficient PV device, the uniformity of the active layer is another important factor to be considered since non-uniform PV thin film deposition over the nanostructure can be problematic to the device performance. Leung et al. reported an a-Si:H thin film solar cell fabricated on aluminum nanospike (NSP) that can remarkably improve the photon capturing capability and resulted in a PCE of over 8.4%.^[37] Nonetheless, it was also found that an NSP with an excessively high aspect ratio will cause a degraded PV performance due to the non-uniform deposition of PV thin film at the NSP sidewall. Shown in Figure 3e is the cross-sectional SEM image of a NSP-based thin film solar cell with a NSP height of around 1200 nm, which is the highest aspect ratio in the comparison. From the SEM image, it can be clearly seen that the a-Si:H thickness at the NSP sidewall is only half of the thickness at the tip, which is caused by the directionality of PECVD deposition and leads to non-uniform coverage of a-Si:H film. The reduced PV performance due to the nonuniform coverage of a-Si:H was also supported by device simulation done by Silvaco Atlas. Figure 3f shows simulated J-V characteristic of PV devices with three different a-Si:H thicknesses at the sidewall of the NSP. As shown in Figure 3f, both $V_{\rm oc}$ and $J_{\rm sc}$ decrease dramatically with the reduction of the sidewall a-Si:H thickness, which is consistent with the experimental results. To sum up, these works clearly demonstrate the importance of considering the influences of nanostructures on carrier dynamics and electrical properties of active materials, such as increased junction area and depletion region trap density, due to introducing nanostructures.



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Also, the utilization of excessively high an aspect ratio of nanostructures in solar energy harvesting devices can have a significant detrimental effect on the electrical properties of active materials, including localized defect and thin-film thickness uniformity.

4.2. Increased Recombination Arising from Additional Surface Area

As discussed in the previous sections, nanostructures can substantially improve the light trapping capabilities and performance of solar energy harvesting devices. On the other hand, the utilization of nanostructures will, however unavoidably, increase the surface area of devices. Therefore, an increase of surface recombination is a natural consequence and this factor should be considered for device optimization since surface recombination can have a significant impact on both $J_{\rm sc}$ and $V_{\rm oc}$. Assuming the highest generation region of photo-carriers is at the top surface of solar cells, a high surface recombination rate has an especially detrimental impact on the J_{sc} of solar cells. Notably, surface recombination is related to dangling bonds, the number of which can be reduced by passivation of the surface using silicon dioxide or silicon nitride for crystalline silicon solar cells.^[40,85] In addition, surface recombination can also be reduced by increasing the doping level near the top contact. On the downside, high

level doping can also decrease the carrier diffusion length and cause severe Auger recombination in the case of silicon solar cells.^[86-90] To shed light on the recombination mechanisms related to the increased surface area of nanostructured PV devices, an enormous amount of work has been done.^[40] For example, J. Oh et al. reported an 18.2% efficient black silicon solar cell achieved by controlling the carrier recombination in the device.^[41] In this work, they demonstrated that a nanostructured silicon solar cell has two competing charge recombination processes, namely surface recombination and Auger recombination. Moreover, the dominant mechanism depends on both the *p-n* junction formation conditions and the surface area. Intriguingly, it was found that not only surface recombination but also Auger recombination associated with a high surface area will limit the photo-generated charge collection of nanostructured silicon solar cells. Displayed in Figure 4a is the cross-sectional SEM image of a silicon solar cell with a surface nanostructure fabricated by TMAH (tetramethylammonium hydroxide) solution treatment. Figure 4b shows the carrier lifetime dependence on sheet resistance and surface area. Region I in Figure 4b shows the situation with a doping concentration higher than $1 \times 10^{18} \text{ cm}^{-3}$ in which Auger recombination normally dominates the recombination process and causes a short lifetime and high surface recombination velocity in heavily doped emitters. Also, sheet resistance increases with the decrease of doping concentration. Region II and region III illustrate the situation



Figure 4. a) Cross-sectional SEM image of nanostructured silicon solar cells treated with TMAH solution for 30 s after metal-assisted etching. b) Effective carrier lifetime τ_{eff} of polished and nanostructured silicon. Region I, II and III delineate three different regimes of lifetime determined by sheet resistance. c) Effective surface recombination velocity S_{eff}^{F} with dashed lines as guides to the eye. The solid brown line is a linear fit to Region III data. Color-coded symbols and lines indicate the emitter doping strength: orange, maroon and brown for Region I, II and III, respectively.^[41] d) A diffused and oxidized rantex surface illustrating how the diffusion and its associated depletion region might not conform to the textured surface.^[40] Reproduced with permission.^[41] Copyright 2012, Nature Publishing Group. Reproduced with permission.^[40] Copyright 2009, American Institute of Physics.

with moderate and low doping concentrations, respectively. Figure 4c shows the effective surface recombination velocity $S_{\rm eff}^F$ with respect to the surface area enhancement ratio A^{F}/A_{proj} , where A^{F} and A_{proj} are the front surface area and projected area of the nanostructures, respectively. Evidently, S_{eff}^F increased with A^F/A_{proj} in all doping regions. However, it is worth noting that for heavily doped region I, S_{eff}^F became independent of the total surface area when A^{F}/A_{proj} was larger than 3.8. This means that for a heavily doped and highly textured surface, recombination is not mainly determined by surface recombination. Similar trends were also revealed by K. R. McIntosh and L. P. Johnson that with increased surface area caused by textured surface, small increases in recombination occurs when the surface is heavily doped due to the fact that Auger recombination was dominant. While in the case of lightly doped surface, large recombination was observed and was dominated by Shockley-Read-Hall recombination, making the latter critically depend on the surface area and surface state density.^[40] Notably, for highly doped samples, the relative change in recombination was less than the relative change in surface area, which was caused by the non-conformal diffusion. Figure 4d shows how the diffusion and its associated depletion region might not conform to the textured surface. These results show that surface recombination plays a crucial role to the nanostructured solar cell performance and needs to be considered during optimization.



4.3. Parasitic Absorption in Nanostructured Solar Energy Harvesting Devices

While nanostructures can improve the overall optical absorption of solar energy harvesting devices, it is important to examine how much absorption occurs in the active laver which directly leads to photocurrent. In most devices, there is parasitic light absorption in passive layers including holding substrate and electrodes which cannot contribute to photocurrent. For instance, parasitic absorption in the transparent conducting oxide (TCO) and back reflector of a thin film solar cell generally has no contribution to the output photocurrent. J. Wallentin et al. reported InP nanowire array solar cells with a 13.8% efficiency, and studied the light absorption in different layers of the device structure.^[43] Figure 5a is the cross sectional SEM image of the InP solar cells with the inset diagram showing the axial *n-i-p* axial junctions. Figure 5b illustrates the light absorption and the corresponding current density versus different nanowire diameters. Clearly, absorption in the TCO took up a large portion of the light power, which cannot be neglected. Unfortunately, this portion of light absorption does not contribute to power output. Likewise, absorption in the top *n*-type segment cannot contribute to power output either. Furthermore, the longer the top *n*-type segment was, the lower the short circuit current that was observed. In the analysis of parasitic absorptions, simulation showed its strength in calculating absorptions in different



Figure 5. a) SEM image of processed NWs. The superimposed schematics illustrate the silicon oxide (SiO_X, blue), TCO (red), and the p-i-n doping layers in the NWs. b) Simulated absorbed light as a fraction of the solar spectrum above the InP band gap, and calculated J_{sc} versus NW diameter.^[43] c) SEM characterization of 330 nm a-Si:H solar cells. The scale bar represents 500 nm. d) Contour plot of calculated absorption in each layer in patterned device with absorbing layer of 330 nm.^[16] Reproduced with permission.^[43] Copyright 2012, American Association for the Advancement of Science. Reproduced with permission,^[16] Copyright 2013, Royal Society of Chemistry.



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layers. H. Huang et al. studied thin-film a-Si:H solar cells with low cost nanodent plasmonic substrates and utilized experiments and simulations to analyze the broadband absorption enhancement.^[16] Figure 5c exhibits the SEM image of the 330 nm thick a-Si:H device and figure 5d is its absorption spectrum. Although the nanotextured devices had an overall broadband absorption enhancement, the parasitic absorptions in the ITO layers and especially the back reflector Ag layers were increased at the same time. Overall, it is important to analyze the parasitic absorption in a nanostructured PV device and confirm that light absorption in the active layer is enhanced when utilizing the nanostructure. And this active layer absorption enhancement is preferred to be more than that in the passive layers. That is to say, parasitic absorption should be minimized in order to make full use of the solar power absorbed in nanostructured devices. In order to achieve this goal, both device modeling and experiments should be coupled together.

4.4. Distribution of Photo-Generated Carrier

In order to comprehensively understand light trapping mechanisms and carrier dynamics in solar energy harvesting devices, optical and device simulations have often been utilized to investigate the nanostructured solar energy harvesting devices. The generation rate gives the number of electrons generated in the device resulted by the absorption of photons. In general, light absorption depends on the absorption coefficient and the thickness of the active materials. Intriguingly, the optical generations are always distributed non-uniformly in absorber materials of nanostructured devices. Guo et al. investigated thin-film a-Si:H solar cells based on nanodent plasmonic substrates with a coupled optical and electrical modeling method.^[44] By comparing the electric fields and current densities in planar and nanostructured devices, they proved that the relatively weak electric field localized in the device top corners would lead to a local current reversal and thus cause a reduction of V_{oc} . The regions with different electric fields can be regarded as sub-cells that compose the whole cell in parallel or series. The weaker electric field regions are preferred for the initiation of current reversal under a forward bias and finally cause the decrease of V_{oc} . As a result, the V_{oc} of a patterned cell mainly depends on the regions with the lowest electric field. Figure 6a illustrates the electric field distribution of a nanostructured solar cell under 0.8 V forward bias (p doping concentration: 3×10^{18} cm⁻³) and the electric fields in the corners are relatively weak. Figure 6b shows the current density distribution with arrows indicating the directions of the current density. In the corners with a weak electric field, a local current reversal occurs, which is clearly shown by the reversed arrow directions. The researchers also demonstrated that under a higher p doping concentration $(8 \times 10^{18} \text{ cm}^{-3})$, weak electric field regions will still exist but are not significant enough to cause the current reversal. In other words, non-uniform electric field distribution in nanostructured solar cells is a great limitation to V_{oc} and should be taken into consideration during device optimization.

small

Besides the effect of non-uniform electric field distribution on V_{oc}, the light absorption distribution in the intrinsic layer and doping layers will also affect the electrical performance of solar cells. Deceglie et al. studied p-i-n a-Si:H devices and came up with a critical factor, namely the ratio of absorption in the intrinsic layer over that in all the *p-i-n* layers.^[45] And they demonstrated that nanostructures could be tailored to minimize optical generation distribution in the doped layers, thus improving carrier collection efficiency. Nanostructures with different configurations such as conformal Ag and conformal AZO were studied with simulations. Figure 6c and 6d illustrate the specific structures of these two devices and show the optical generation profiles at 650 nm wavelength where the conformal Ag device has a larger current density than the conformal AZO device. They explained that this current density difference comes from the difference in the ratio K_i/K which denotes the ratio of absorption in the intrinsic layer over that in all the *p-i-n* layers. The reason is that photo-generated carriers in the doped region do not contribute to the photocurrent. So in this p-i-n a-Si:H solar cell configuration, the minimization of optical generation distribution in the doped region became the dominant effect. Besides the PV device, PEC water splitting is another technology used to harvest solar energy to convert water into hydrogen fuel. Qiu et al. reported a PEC water splitting device based on an engineered design of a nanospike (NSP) template. As shown in Figure 6e, NSP can remarkably improve the efficiencies of water splitting as compared to the flat control device due to the improved light trapping effect. This result can further be explained by the photon absorption distribution in the planar and NSP devices shown in Figure 6f1 and 6f2, respectively. In the case of the NSPbased device, other than the enhanced photon absorption indicated by the "hot spots", it can be seen that the photon absorption distribution is rather uniform as compared with other solar water splitting based on other hierarchical structures.^[91] Notably, the uniform distribution of photo-generated carriers in the NSP-based device is highly preferable to compensate the low rate constant of water oxidation and a short minority carrier diffusion length, which resulted in superior conversion efficiency.

5. Summary

Light management by nanomaterials and nanostructures holds promising potency to enhance the performance of solar energy harvesting devices. Light absorbing materials in nanostructured solar energy harvesting devices can absorb an equivalent amount of light with thinner thicknesses as compared to their planar counterpart, thus the collection length of the photo-generated carrier was shortened. In addition, structural designs such as the radial p-n junction and nanostructured electrode can also improve both light trapping and photo-carrier collection. Here, we have summarized the progress of nanostructured solar energy harvesting devices including different structural designs and the utilization of nanostructured electrodes with improved power conversion efficiencies. Additionally, a number reviews





Figure 6. a) Electric field, and b) current density profiles of nanopatterned solar cells under 0.8V forward bias (p-layer doping concentration: 3×10^{18} cm⁻³). The arrows in the figures indicate the directions of electric field and current density.^[44] The generation rate from 650 nm light calculated for the c) conformal AZO, and d) conformal Ag structures plotted on a logarithmic scale, showing that the performance enhancement in the conformal Ag structure comes from an optical mode with an improved K_i/K ratio for 650 nm incident light resulting in improved EIQE at that wavelength. The dashed lines indicate the edges of the doped a-Si:H regions.^[45] e) J-V curves of the Ti-doped hematite photoelectrodes based on the three different NSP arrays, showing the best performance achieved with the 3D NSP array photoelectrode with a pitch of 1000 nm. f) Crosssectional photon absorption profile of device on planar and NSP substrate. Red color hot area representing high generation indicating effective light trapping by NSP.^[46] Reproduced with permission.^[44] Copyright 2014, Elsevier. Reproduced with permission.^[45] Copyright 2012, American Chemical Society.

of literature works reported that improper design can be detrimental to the performance of nanostructured device and therefore optimization of different key aspects are needed in order to achieve highly efficient solar energy harvesting. In this review article, we organized and discussed the works on the design rule of nanostructured solar energy harvesting devices, including PV thin films non-uniformity on nanostructures, increased surface recombination due to nanostructures, parasitic absorption, and the importance of uniform distribution of photo-generated carriers. Understanding and the establishment of these design rules can eventually benefit the rational design of high performance solar energy harvesting devices with practical applications in the future.

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- [1] M. A. Green, Prog. Photovoltaics Res. Appl. 2002, 10, 235.
- [2] E. Yablonovitch, G. D. Cody, Electron Devices, *IEEE Transactions on* **1982**, *29*, 300.
- [3] R. Yu, Q. Lin, S. F. Leung, Z. Fan, Nano Energy 2012, 1, 57.
- [4] R. Kapadia, Z. Fan, A. Javey, Appl. Phys. Lett. 2010, 96, 103116.
- [5] R. Kapadia, Z. Fan, K. Takei, A. Javey, Nano Energy 2012, 1, 132.
- [6] B. Hua, Q. Lin, Q. Zhang, Z. Fan, *Nanoscale* **2013**, *5*, 6627.
- [7] Q. Lin, H. Huang, Y. Jing, H. Fu, P. Chang, D. Li, Y. Yao, Z. Fan, J. Mater. Chem. C 2014, 2, 1233.
- [8] S. Leung, Q. Zhang, F. Xiu, D. Yu, J. C. Ho, D. Li, Z. Fan, J. Phys. Chem. Lett. 2014, 5, 1479.
- [9] D. Liang, Y. Kang, Y. Huo, Y. Chen, Y. Cui, J. S. Harris, Nano Lett. 2013, 13, 4850.
- [10] J. He, P. Gao, M. Liao, X. Yang, Z. Ying, S. Zhou, J. Ye, Y. Cui, ACS Nano 2015, 9, 6522.
- [11] M. M. Tavakoli, K. Tsui, S. Leung, Q. Zhang, J. He, Y. Yao, D. Li, Z. Fan, ACS Nano 2015, 9, 10287.
- [12] S. F. Leung, M. Yu, Q. Lin, K. Kwon, K. L. Ching, L. Gu, K. Yu, Z. Fan, *Nano Lett.* **2012**, *12*, 3682.
- [13] Q. Lin, B. Hua, S. Leung, X. Duan, Z. Fan, ACS Nano 2013, 7, 2725.
- [14] R. Yu, K. Ching, Q. Lin, S. Leung, D. Arcrossito, Z. Fan, *ACS Nano* **2011**, *5*, 9291.
- [15] M. H. Lee, N. Lim, D. J. Ruebusch, A. Jamshidi, R. Kapadia, R. Lee, T. J. Seok, K. Takei, K. Y. Cho, Z. Y. Fan, H. Jang, M. Wu, G. J. Cho, A. Javey, *Nano Lett.* **2011**, *11*, 3425.
- [16] H. Huang, L. Lu, J. Wang, J. Yang, S. Leung, Y. Wang, D. Chen, X. Chen, G. Shen, D. D. Li, Z. Fan, *Energy Environ. Sci.* 2013, *6*, 2965.
- [17] B. Hua, B. Wang, M. Yu, P. W. Leu, Z. Fan, *Nano Energy* **2013**, *2*, 951.
- [18] Q. Lin, S. Leung, K. Tsui, B. Hua, Z. Fan, *Nanoscale Res. Lett.* **2013**, *8*, 268.
- [19] K. H. Tsui, Q. Lin, H. Chou, Q. Zhang, H. Fu, P. Qi, Z. Fan, Adv. Mater. 2014, 26, 2805.
- [20] Q. Lin, S. Leung, L. Lu, X. Chen, Z. Chen, H. Tang, W. Su, D. Li, Z. Fan, ACS Nano 2014, 8, 6484.
- [21] Y. L. Chueh, Z. Y. Fan, K. Takei, H. Ko, R. Kapdia, A. Rathore, N. Miller, K. Yu, M. Wu, E. E. Haller, A. Javey, *Nano Lett.* **2010**, *10*, 520.
- [22] I. J. Kramer, D. Zhitomirsky, J. D. Bass, P. M. Rice, T. Topuria,
 L. Krupp, S. M. Thon, A. H. Ip, R. Debnath, H. Kim, *Adv. Mater.* **2012**, *24*, 2315.
- [23] J. Kim, H. J. Choi, K. Park, R. E. Cohen, G. H. McKinley, G. Barbastathis, *Small* **2014**, *10*, 2487.
- [24] H. Lin, H. Cheung, F. Xiu, F. Wang, S. Yip, N. Han, T. Hung, J. Zhou, J. C. Ho, C. Wong, J. Mater. Chem. A 2013, 1, 9942.
- [25] S. Jeong, E. C. Garnett, S. Wang, Z. Yu, S. Fan, M. L. Brongersma, M. D. McGehee, Y. Cui, *Nano Lett.* **2012**, *12*, 2971.
- [26] J. Kim, A. J. Hong, J. Nah, B. Shin, F. M. Ross, D. K. Sadana, ACS Nano 2012, 6, 265.
- [27] B. Wang, P. W. Leu, Nanotechnology 2012, 23, 194003.
- [28] K. X. Wang, Z. Yu, V. Liu, Y. Cui, S. Fan, *Nano Lett.* **2012**, *12*, 1616.
- [29] Y. Xie, B. Cai, D. Yu, W. Shan, W. Zhang, J. Cryst. Growth 2012, 346, 64.
- [30] J. Xiao, L. Xu, L. Geng, L. Tong, F. Yang, J. Xu, W. Su, D. Liu, Y. Yu, Z. Ma, *Appl. Surf. Sci.* **2011**, *257*, 10893.
- [31] J. Zhu, C. Hsu, Z. Yu, S. Fan, Y. Cui, Nano Lett. 2010, 10, 1979.
- [32] C. Hsu, S. T. Connor, M. X. Tang, Y. Cui, Appl. Phys. Lett. 2008, 93, 133109.

- [33] Z. Y. Fan, H. Razavi, J. W. Do, A. Moriwaki, O. Ergen, Y. L. Chueh, P. W. Leu, J. C. Ho, T. Takahashi, L. A. Reichertz, S. Neale, K. Yu, M. Wu, J. W. Ager, A. Javey, *Nat. Mater.* **2009**, *8*, 648.
- [34] B. M. Kayes, H. A. Atwater, N. S. Lewis, J. Appl. Phys. 2005, 97, 114302.
- [35] M. M. Adachi, A. J. Labelle, S. M. Thon, X. Lan, S. Hoogland, E. H. Sargent, *Sci. Rep.* **2013**, *3*, 2928.
- [36] M. M. Tavakoli, A. Simchi, Z. Fan, H. Aashuri, *Chem. Commun.* 2015.
- [37] S. Leung, L. Gu, Q. Zhang, K. Tsui, J. Shieh, C. Shen, T. Hsiao, C. Hsu, L. Lu, D. Li, Q. Lin, Z. Fan, *Sci. Rep.* **2014**, *4*, 4243.
- [38] C. Hsu, C. Battaglia, C. Pahud, Z. Ruan, F. Haug, S. Fan, C. Ballif, Y. Cui, Adv. Energy Mater. 2012, 2, 628.
- [39] C. Battaglia, C.- Hsu, K. Söderström, J. Escarré, F.-J. Haug, M. Charrière, M. Boccard, M. Despeisse, D. T. L. Alexander, M. Cantoni, Y. Cui, C. Ballif, ACS Nano 2012, 6, 2790.
- [40] K. R. McIntosh, L. P. Johnson, J. Appl. Phys. 2009, 105, 124520.
- [41] J. Oh, H. Yuan, H. M. Branz, Nat. Nanotechnol. 2012, 7, 743.
- [42] J. A. Czaban, D. A. Thompson, R. R. LaPierre, Nano Lett. 2009, 9, 148.
- [43] J. Wallentin, N. Anttu, D. Asoli, M. Huffman, I. Aberg, M. H. Magnusson, G. Siefer, P. Fuss-Kailuweit, F. Dimroth, B. Witzigmann, H. Q. Xu, L. Samuelson, K. Deppert, M. T. Borgstrom, *Science* 2013, *339*, 1057.
- [44] R. Guo, H. Huang, P. Chang, L. Lu, X. Chen, X. Yang, Z. Fan, B. Zhu, D. Li, *Nano Energy* **2014**, *8*, 141.
- [45] M. G. Deceglie, V. E. Ferry, A. P. Alivisatos, H. A. Atwater, Nano Lett. 2012, 12, 2894.
- [46] Y. Qiu, S. Leung, Q. Zhang, B. Hua, Q. Lin, Z. Wei, K. Tsui, Y. Zhang, S. Yang, Z. Fan, *Nano Lett.* **2014**, *14*, 2123.
- [47] S. Jeong, M. D. McGehee, Y. Cui, Nat. Commun. 2013, 4, 2950.
- [48] Y. Wang, N. Lu, H. Xu, G. Shi, M. Xu, X. Lin, H. Li, W. Wang, D. Qi, Y. Lu, *Nano Res.* **2010**, *3*, 520.
- [49] C. M. Hsu, C. Battaglia, C. Pahud, Z. Ruan, F. J. Haug, S. Fan, C. Ballif, Y. Cui, Adv. Energy Mater. 2012, 2, 628.
- [50] J. Zhu, Z. Yu, G. F. Burkhard, C. Hsu, S. T. Connor, Y. Xu, Q. Wang, M. McGehee, S. Fan, Y. Cui, *Nano Lett.* **2008**, *9*, 279.
- [51] K. Cho, D. J. Ruebusch, M. H. Lee, J. H. Moon, A. C. Ford, R. Kapadia, K. Takei, O. Ergen, A. Javey, *Appl. Phys. Lett.* **2011**, *98*, 203101.
- [52] E. C. Garnett, P. D. Yang, J. Am. Chem. Soc. 2008, 130, 9224.
- [53] M. D. Kelzenberg, D. B. Turner-Evans, B. M. Kayes, M. A. Filler, M. C. Putnam, N. S. Lewis, H. A. Atwater, *Nano Lett.* **2008**, *8*, 710.
- [54] T. J. Kempa, B. Tian, D. R. Kim, J. Hu, X. Zheng, C. M. Lieber, Nano Lett. 2008, 8, 3456.
- [55] S. H. Ko, D. Lee, H. W. Kang, K. H. Nam, J. Y. Yeo, S. J. Hong, C. P. Grigoropoulos, H. J. Sung, *Nano Lett.* **2011**, *11*, 666.
- [56] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. D. Yang, Nat. Mater. 2005, 4, 455.
- [57] G. Mariani, Z. Zhou, A. Scofield, D. L. Huffaker, *Nano Lett.* **2013**, *13*, 1632.
- [58] J. Tang, Z. Huo, S. Brittman, H. Gao, P. Yang, Nat. Nanotechnol. 2011, 6, 568.
- [59] F. Wang, Q. Yang, G. Xu, N. Lei, Y. Tsang, N. Wong, J. C. Ho, *Nanoscale* **2011**, *3*, 3269.
- [60] Y. S. Zhou, K. Wang, W. Han, S. C. Rai, Y. Zhang, Y. Ding, C. Pan, F. Zhang, W. Zhou, Z. L. Wang, ACS Nano 2012, 6, 6478.
- [61] K. Zhu, N. R. Neale, A. Miedaner, A. J. Frank, *Nano Lett.* 2007, 7, 69.
- [62] Z. Yin, S. Wu, X. Zhou, X. Huang, Q. Zhang, F. Boey, H. Zhang, Small 2010, 6, 307.
- [63] Z. Y. Fan, R. Kapadia, P. W. Leu, X. B. Zhang, Y. L. Chueh, K. Takei, K. Yu, A. Jamshidi, A. A. Rathore, D. J. Ruebusch, M. Wu, A. Javey, *Nano Lett.* **2010**, *10*, 3823.
- [64] H. Wang, K. Lai, Y. Lin, C. Lin, J. He, Langmuir 2010, 26, 12855.
- [65] Y. Lin, K. Lai, H. Wang, J. He, Nanoscale 2010, 2, 2765.
- [66] Y. Lin, H. Wang, C. Lin, J. He, J. Appl. Phys. 2009, 106, 114310.

reviews



- [67] S. Tsai, H. Chang, H. Wang, S. Chen, C. Lin, S. Chen, Y. Chueh, J. He, ACS Nano 2011, 5, 9501.
- [68] K. Peng, X. Wang, L. Li, X. Wu, S. Lee, J. Am. Chem. Soc. 2010, 132, 6872–6873.
- [69] S. E. Han, G. Chen, Nano Lett. 2010, 10, 1012.
- [70] J. Li, Y. Qiu, Z. Wei, Q. Lin, Q. Zhang, K. Yan, H. Chen, Z. Fan, S. Yang, *Energy Environ. Sci.* 2014, 7, 3651.
- [71] L. Li, J. Opt. Soc. Am. 1997, 14, 2758.
- [72] V. Liu, S. Fan, Comput. Phys. Commun. 2012, 183, 2233.
- [73] S. G. Tikhodeev, A. Yablonskii, E. Muljarov, N. Gippius, T. Ishihara, *Phys. Rev. B* **2002**, *66*, 045102.
- [74] M. Fickenscher, T. Shi, H. E. Jackson, L. M. Smith, J. M. Yarrison-Rice, C. Zheng, P. Miller, J. Etheridge, B. M. Wong, Q. Gao, *Nano Lett.* **2013**, *13*, 1016.
- [75] M. H. Lee, K. Takei, J. Zhang, R. Kapadia, M. Zheng, Y. Chen, J. Nah, T. S. Matthews, Y. Chueh, J. W. Ager, *Angew. Chem. Int. Ed.* 2012, *124*, 10918.
- [76] T. Song, F. Zhang, X. Lei, Y. Xu, S. Lee, B. Sun, *Nanoscale* **2012**, *4*, 1336.
- [77] H. Wang, K. Tsai, K. Lai, T. Wei, Y. Wang, J. He, *Opt. Express* **2012**, 20, A94.
- [78] Y. Rosenwaks, L. Burstein, Y. Shapira, D. Huppert, *Appl. Phys. Lett.* **1990**, *57*, 458.
- [79] J. Oh, T. G. Deutsch, H. Yuan, H. M. Branz, *Energy Environ. Sci.* 2011, 4, 1690.

- [80] A. Mavrokefalos, S. E. Han, S. Yerci, M. S. Branham, G. Chen, *Nano Lett.* 2012, 12, 2792.
- [81] J. Kim, C. Battaglia, M. Charrière, A. Hong, W. Jung, H. Park, C. Ballif, D. Sadana, Adv. Mater. 2014, 26, 4082.
- [82] D. Liang, Y. Huo, Y. Kang, K. X. Wang, A. Gu, M. Tan, Z. Yu, S. Li, J. Jia, X. Bao, *Adv. Energy Mater.* **2012**, *2*, 1254.
- [83] M. Python, O. Madani, D. Dominé, F. Meillaud, E. Vallat-Sauvain, C. Ballif, Sol. Energy Mat. Sol. Cells 2009, 93, 1714.
- [84] M. G. Deceglie, V. E. Ferry, A. P. Alivisatos, H. A. Atwater, *IEEE J. Photovolt.* 2013, 3, 599.
- [85] E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz, J. R. Durrant, J. Am. Chem. Soc. 2003, 125, 475.
- [86] S. Olibet, E. Vallat-Sauvain, C. Ballif, Phys. Rev. B 2007, 76, 035326.
- [87] A. K. Sharma, S. K. Agarwal, S. N. Singh, Sol. Energy Mat. Sol. Cells 2007, 91, 1515.
- [88] V. I. Klimov, J. Phys. Chem. B 2006, 110, 16827.
- [89] A. N. M. Green, E. Palomares, S. A. Haque, J. M. Kroon, J. R. Durrant, J. Phys. Chem. B 2005, 109, 12525.
- [90] A. J. Sabbah, D. M. Riffe, J. Appl. Phys. 2000, 88, 6954.
- [91] A. Kay, I. Cesar, M. Graetzel, J. Am. Chem. Soc. 2006, 128, 15714.

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