Chapter

Periodic Nanophotonic Structures-Based Light Management for Solar Energy Harvesting

Nikhil Deep Gupta

Abstract

Solar energy has always been an obvious choice for solving the energy issues for the humans for centuries. The two most popular choices, out of many, to harness this infinite source of energy are: solar cells and photoelectrochemical cells. Although both these techniques are quite attractive, they have inherent limitations for tapping all of the incident photons. Maximizing the absorption of incident photons to produce maximum possible electrical output is always the main impetus for the researchers working to streamline these two techniques and making them compatible with existing sources of electrical energy. It has been well established that the light trapping in the solar cells and photoelectrochemical cells can play a vital role in improving their performance. To design light harvesting structures for both these applications, periodic nanophotonic structures have demonstrated stupendous results and shown that they have the real potential to enhance their performance. The chapter, in this regard, presents and reviews the current and historical aspects of the light harvesting structures for these two interesting applications and also discusses about the future of the research to further the performance of these large-area solar-to-electrical conversion transducers.

Keywords: periodic nanophotonic structures, solar cells, photoelectrochemical cells, photonic band gap, diffraction grating

1. Introduction

As per the United Nations Foundation report [1], one of the major crises the world currently is facing is the climate change and sustainable energy solution. For sustainable development and to curb climate-related problems and at the same time for catering to the ever-increasing energy demands of the humans, more and more countries are shifting toward renewable energy sources. The factor, in turn, drives the development for the future access to affordable and sustainable energy through investment in the efficient renewable energy programs, such as Jawaharlal Nehru National Solar Mission program [2] in India, which is one of the largest programs currently running in the world for renewable energy expansion.

Most part of the world is poised to have the solar energy available and that too for maximum part of the year. Also, it is an infinite source of energy that is freely available and that too without causing any environment adversaries. The energy from the sun plays the most important role in the sustenance of life on the earth as almost all the energy sources available here are inherent from the heat and light of the sun itself, either directly or indirectly. The solar energy is being in use from thousands of years through various ways. Still, this vast source of energy is underutilized and, thus, novel and innovative practices are required to harness this unending source of energy. The total solar energy received on the surface of the earth is accounted to about 3,850,000 EJ/year [3] and it is more than twice the total energy that can be ever gained from all of the earth's nonrenewable energy resources combined. Hence, harnessing the solar energy for the betterment of the society has always attracted the researchers.

To tap the solar energy, many applications are being done, starting from the solar thermal innovations to the solar photovoltaics applications. Out of them, direct conversion of the solar incidence to the electrical energy is one of the prominent reasons for the immense increase in the popularity of the solar energy related applications. Two of the most prominent techniques that directly convert the solar energy into the electrical energy are the solar cells (SCs) and the photoelectrochemical cells (PECs). The research and innovations in these optoelectronic devices have regained interest during the last two decades or so, on account of their proven capability to effectively harness the solar energy. The task is to make them compatible and competitive with the available energy resources.

A simplistic design of a complete SC is shown in **Figure 1**. The principle of operation of SC is well known for years [4], and they can work satisfactory for long without much requirement of maintenance. The operation of a SC can be summed up in three processes that include carrier generation upon incidence of light, carrier separation, and carrier collection at the outer electrodes [4]. The generation of charge carriers occurs in the active region, which is of the materials, which on absorption of a photon generate electron-hole pairs. The absorption in the active material is only responsible for the useful charge carrier generation. These generated charge carriers are then separated because of a built-in electric field provided through designs such as p-n junction and then are effectively collected at the outer electrodes.

The reflections from the top account for more than 30% of the losses from a SC. To reduce these reflections, an antireflection coating (ARC) is placed at the top as an integral part of the design of a SC. On the other front, to reduce the transmission of the unabsorbed photons from the active layer (AL), back reflectors (BRs) are being employed to reflect back these unattended photons. Commonly, both ARC and BR are considered as a part of light management schemes (LMSs) for the SC. Although, the incorporation of LMS increases the cost and complexity of the overall device, the performance enhancement that they provide helps to reduce

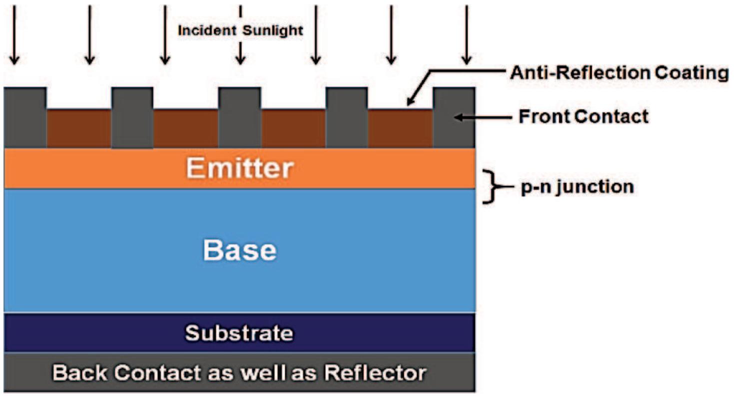

Figure 1.
A basic structure of a solar cell.

the final cost-to-efficiency (CE) ratio of these devices. The LMS structures play a very critical role in the SC designs and are becoming even more crucial with the reducing thickness of the ALs in the novel designs.

On the other hand, solar-to-electricity conversion through chemical route using PEC process is also becoming significant due to its capability of long-term energy storage without adversely affecting the environment. PEC uses to generate hydrogen through water splitting using solar energy, also commonly known as photo-electrolysis. The created free hydrogen due to photo-electrolysis can then be utilized for various applications. In a commonly used PEC design, there are two electrodes, namely, a working photo-anode and a counter metal-electrode as shown in **Figure 2** (although three electrodes' design is also being used, with the third electrode known as reference electrode). The photo-anode acts as a photocatalyst that absorbs the photons from the solar flux incident on it and creates charge carriers. Then, these carriers move to the opposite polarity electrodes that leads to the generation of the electrical energy.

In both of the abovementioned energy harvesting operations using optoelectronic devices, the main aspect that one looks toward to define their quantitative performance is their photo-conversion efficiency (PCE). The recent past has observed a considerable improvement in the PCE for these devices. In the case of SC, this pace of increase in the PCE is even faster as compared to PEC. For a crystalline Si-SC, the efficiency has almost reached to the limiting values [5, 6], whereas for PEC the efficiency is well under 20% [7]. However, there is still a gap that is required to be filled before these devices can certainly overtake their conventional energy counterparts. One of the most important parameters that affects these devices' mass acceptance is their CE ratio.

To reduce the CE ratio, it is obvious that either one has to reduce the cost of design or increase the PCE, or one can target both. One of the ways to reduce cost is to go for thin film technologies for design. However, it has a trade-off as such designs adversely affect the PCE. In order to compensate for the losses incurred, one of the time-tested methods is the use of LMS. The chapter is devoted to the discussions related to the design and innovations for the LMS for these solar energy harvesting optoelectronic devices. The LMS makes it possible for both SC and PCE structures to notably improve their PCE. Nanophotonics structures are playing a very crucial and successful role in designing LMS, and it has been demonstrated through several studies that they have a realistic potential to make these devices to work at their limiting values or can even go beyond that.

The chapter is organized as follows: Section 2 discusses about the need for LMS for solar optoelectronic devices. The role that periodic nanophotonic structures can play is discussed in Section 3. That section also deals with the recent advancements

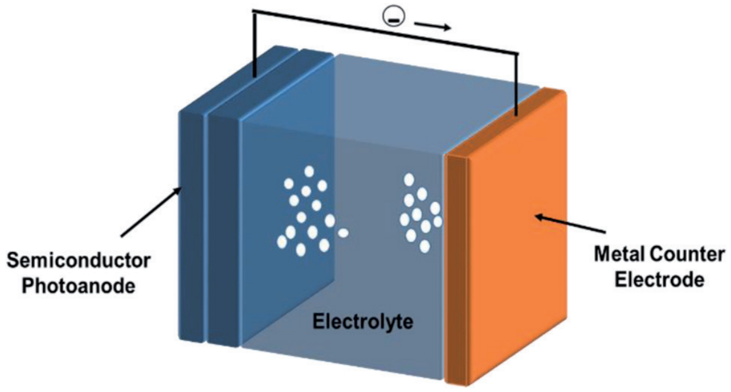

Figure 2.
A basic structure of a photoelectrochemical cell with two electrodes.

and innovations related to LMS in the field of SC and PEC, respectively. Section 4 discusses the present challenges and future perspective related to the mentioned optoelectronics devices followed by concluding remarks.

2. Need of light management for solar optoelectronic devices

From past few decades, it has been demonstrated that the thin film (TF) technologies have the reasonable capability to perform the operation of optoelectronics solar energy harvester (OSEH) with an additional advantages of low cost, lightweight, flexibility, comparatively easier fabrication processing, and higher production throughput [8]. To make the CE ratio of these OSEH comparable with the existing technologies, the ALs' thicknesses used in these devices are becoming thinner and thinner, as it can check the design cost. Although, the reduction in the thickness of ALs control the overall design cost, the final device has to compromise with the PCE, as with reduction in thickness, the number of photons that can be absorbed in an AL are also get restricted [4, 9]. The restriction is due to the fact that each material has its own absorption coefficient that dictates the incident photons' absorption within its layer's specified thickness, and if the material thickness is lesser than that, the photon remains unattended and can pass through the device unabsorbed without any useful contribution. In other words, the photon gets wasted in such a case.

Hence, a large part of the incident spectrum has wasted because of this incomplete absorption. Together with the loss due to limited thickness of the AL, there are also major losses due to reflections from the top surface as well as due to recombination, including others. In such circumstances, to curb these losses and increase the useful absorption of the otherwise lost photons is utmost required to improve PCE of these devices. To enhance the absorption, the most practical and profoundly used technique is light management structure. LMS is the process to effectively couple the incident photon to the AL and make it possible for the layer to successfully absorb it and contribute to the useful charge carrier generation. As the focus of the LMS is to make it possible for an incident photon to be effectively get absorbed within the active material, LMS can be designed in combinations with the ALs in various ways depending upon the material used and the application requirement [10, 11].

The use of ARC at the top of the SC and PEC designs is a part of a LMS, where the main task of ARC is to reduce reflections from the top that arises due to the sudden variation of the refractive index from the incident medium to the absorbing medium. ARC, thus, requires to serve the purpose of index matching for the incident light with the absorbing layers and increase useful absorption of photons [4, 9]. ARC in a simpler design can be carved out as a single planar layer whereas its performance can be improved with the incorporation of multiple layers to provide gradual change in refractive index [12, 13]. In all, the ARC structure must have negligible reflections with insignificant absorption for the incident spectrum. However, practically observing such a property out of the planar ARC design that can achieve supreme coupling without losses throughout the incident spectrum, and ultimately restricts the outward movement of coupled photons from it through oblique escape angles, is really challenging [9]. For planar ARC, there is a need to appropriately find an optimized central wavelength, λ_c, to get relatively low reflections around the prioritized wavelength range. A planar ARC has almost zero reflections at λ_c.

The thickness of the planar ARC design (T_{ARC}) can be optimized with value of λ_c as it is equal to the quarter of the central wavelength. Considering n_{ARC} as the refractive index of the single planar ARC layer, mathematically T_{ARC} is given as

$$T_{ARC} = \frac{\lambda_c}{4n_{ARC}} \tag{1}$$

In contrast, LMS when design at the back of the ALs or when ALs in itself are being used as the LMS, they are intended for increasing the optical path length of the coupled incident photons, virtually through diffraction or scattering in the desired directions, so that they can be absorbed within the limited AL thickness [14, 15]. In such cases, the LMS design is focused for trapping photons that require absorption depth more than the AL thickness to be successfully absorbed in it. The absorption depth requires to tap a photon of certain wavelength depends upon the absorption coefficient of the active material used [4]. The relation between the absorption coefficient, α, and incident photon wavelength, λ is given as:

$$\alpha = {}^{4\pi k}\!/_{\lambda} \tag{2}$$

Here, *k* denotes the materials' refractive index' imaginary part. The absorption depth requires to absorb a particular wavelength photon is given by the inverse of the absorption coefficient. It is clear from the Eq. (2) that as the incident photon wavelength increases, the absorption coefficient decreases and in turn comparatively thicker layers are required to absorb these photons. So, materials with high absorption coefficients should be more preferred for better absorption of incident photons with less thickness. However, for keeping the CE ratio to a lowest possible side and also for creating flexible structures, the thickness of the AL is always kept less than the required thickness for absorbing the possible highest wavelength photons. The case is even worse for Si, the most preferred material for designing SC, as it has very low α values near to its band edge.

In the case of PEC designs, the LMS has an another important role to play. For PEC devices, from last decade or so, Group-III nitride materials, such as $In_xGa_{1-x}N$, have emerged as the leading source for designing photo-electrodes. It is due to the possibility to tune their bandgap over the large wavelength range (from 3.4 to 0.65 eV) (depending upon the concentration of Indium in GaN) [16–18]. With the possibility of tuning the bandgap, the $In_xGa_{1-x}N$ materials seems to have the potential to provide full spectrum operations. Other favorable properties of group-III nitride materials for PEC devices include sufficiently good irradiation resistance chemical tolerance, thermal stability, carrier mobility, direct bandgap property with significantly high absorption coefficient even near to the band edge that make them suitable and a preferred choice over metal oxides for PEC operations [19–21].

Although, $In_xGa_{1-x}N$ seems to be a best fit for the PEC devices, the main limitation is the thickness of its good quality epitaxial film that can be grown over the substrate. This remains one of the unsolved queries for $In_xGa_{1-x}N$, because of which even with many favorable optoelectronics properties, still $In_xGa_{1-x}N$-based designs are not prevalent especially for SC applications. $In_xGa_{1-x}N$ material is basically grown on different kind of substrates that always has a lattice mismatch (sapphire is typically the preferred substrate material for growing III-nitride materials) [22]. To tune the bandgap of $In_xGa_{1-x}N$ to absorb maximum incident solar spectrum, it is required to increase the In incorporation, but with increase in In composition, the quality of grown film degrades. This is due to the increase in defect densities with increase in In incorporation, and in turn, puts a halt on the PCE possible from the $In_xGa_{1-x}N$-based devices [23]. In such a case, LMS as a BR becomes crucial, as it is a support structure that can make the design to achieve high absorption even with limited thickness of active layer with limited In content.

Designing an ideal low loss BR with a planar metallic layer [24] that can perform equal reflections throughout the desired range of wavelengths is a tedious task and practically is not able to achieve even half of the limiting values [25]. Theoretically, it is possible to achieve an enhancement of $4n^2$ in absorption with an ideal LMS (where n denotes refractive index of the active material) [25]. However, with the planar LMS design the limiting values has not been achieved till date because of several factors such as the intrinsic losses from surface plasmon modes generated at the granular metal-dielectric interface [26]. Due to the inherent limitations in absorption enhancement that planar LMS achieve, it becomes imperative for the researchers to look toward the design of low loss, near-to-ideal LMS that can let the development of the OSEH that can work near to the limiting values [6] to get maximum output from the incident sunlight. The possible solution lies in the use of the nanophotonic structures. They have regularly demonstrated their potential for the design of LMS and will be discussed in detail in next section.

3. Periodic nanophotonic structures for light trapping

Now, as it is well established fact that with the commonly used planar ARC and BR structures, it is not ever possible to achieve the limiting PCE values, so it is very much required to look for the better and efficient alternatives to design LMS that can include both random as well as periodic nanostructures. Although, the random structures are easy to fabricate and design with minimum infrastructure requirement, they are complex to reproduce and rescale for the industry required bulk production, it is better to look for the periodic structures for designing LMS. Periodic nanophotonic structures (PNS) having subwavelength dimensions have been utilized and demonstrated their effectiveness successfully for a variety of optoelectronic applications [27–31]. PNS have a lot to offer for the design of optoelectronic devices as they have various unique advantages especially for the OSEH applications. They have been successfully utilized and demonstrated their superiority for designing LMS.

These PNS have the better capability to couple the incident photons to the AL as compared to the planar LMS and thus can help to enhance the charge carrier generation, surface to volume ratio that can boost the quantum effects, reduce recombination that accounts to major losses, enhance carrier collection at electrodes, provide tunable bandgap property etc. [32, 33]. The PNS can be coupled with any of the active material system in use and contribute according to their properties. With unique properties of PNS, one can have the advantage of manipulating the light propagation and light-matter interaction as per requirement and opens up the wide range of possibilities in variety of applications for the field of optics and photonics, including OSEH applications.

These structures can be incorporated in the various ways within the OSEH devices, as per the particular application's requirement. Researchers have examined PNS with OSEH in different forms extending from using them as diffraction element to the back reflector or even carving active material itself as PNS to enhance the absorption of incident photons. The PNS are mainly responsible for taking the PCE of these energy harvesters near to the limiting values or in some cases even surpassed them. In the coming subsections, the article will discuss in detail about the history and advancement that has been done in the field of PNS-based optoelectronics solar energy harvesters, especially SC and PEC.

3.1 Light management through periodic nanophotonic structures in solar cells

Since, the beginning of the current century, the research and development in the field of PNS-based SC designs have seen an upward swing, irrespective of the active material used, starting from Si to perovskites. The fact can be recognized with the exponential increase in the number of research articles that have emerged out of the area. The researchers have conducted studies for the amalgamations of PNS with the SC from different perspectives, as they used them as a single low loss dielectric BR [34], as a diffraction grating [14, 35], designing the absorbing material itself as PNS [36, 37]. These studies are basically performed either using 1D or 2D or pseudo 3D PNS [38–41], as designing and fabrication of 3D PNS is still a challenging task.

In one of the interesting findings, Wang et al. in [42], demonstrated the critical role that PNS has to play for the improvement in the performance of thin film SC and their studies was based on GaAs active material. It is important to highlight the findings because GaAs has better absorption coefficient and radiative recombination dominates as compared to Si and earlier it was thought that the BR could only be important for materials such as Si having less band edge absorption coefficient [25]. In case of GaAs, specially, the BR becomes important to reflect back the unabsorbed photons that are radiatively emitted and let them to contribute through photon recycling. Following the proposal studies, Gupta et.al in [15] proposed a PNS-based GaAs structure, as shown in **Figure 3**, having only 500 nm active layer thickness. They have presented that the PNS having a combination of 2D and 1D structures to provide a pseudo 3D PNS has a capability to provide enhancement of about 46% as compared to the planar LMS design.

Another important point that they presented was that the effect of BR decreases with increase in the AL thickness. They have demonstrated that the enhancement contribution from PNS structures for PCE was about 200% in case of 100-nm active layer cell that reduces to only around 25% for 1-μm thick AL cell. Thus, for thicker cells, the BR role is limited to only near to the band edge wavelengths at most and in such cases, even planar layers can accomplish the task.

Zhou et al. illustrated one of the classical findings for PNS in [14]. They have used a-Si:H as the active material and designed LMS for the same. In the LMS, they have utilized 1D PNS at the back of the SC as distributed Bragg reflectors (DBRs), and in between the active layer and DBR, there was a layer of 2D PNS placed to enhance absorption through diffraction of light at oblique angles. The authors put forth the physical insight of the whole mechanism and emphasized an important condition that the PNS lattice constant must be comparable to the wavelength of light in the medium, which it meant to manipulate.

In another interesting study, Chutinan et al. in [43], for thin crystalline Si-SC, demonstrated that it is possible to notably enhance the device PCE with PNS.

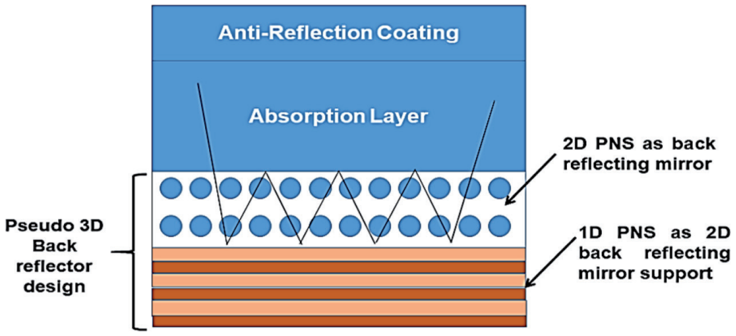

Figure 3.
Schematic design of a SC using pseudo 3D PNS as back reflector.

They have demonstrated the comparative enhancement of around 11 and 3% for 2 and 10 μm active layer thick SC designs, respectively, for Si AL. The SC design was achieved through carving active layer itself as PNS, as shown in **Figure 4**. The article demonstrated a decent physical interpretation of the SC design having PNS-based LMS within absorbing layer. As the PNS can be equally implemented for other material systems, a work has recently also demonstrated the effect of PNS within active layer for perovskite-based design [44]. The results have shown that the PNS are also critical for the design of perovskites-based SC as the defects in the deposited perovskites films becomes prominent with their increasing thickness.

In one of the exciting studies, Munday in [45] presented and analyzed the Si-SC design having LMS targeted from the top coupling surface using the PNS. The PNS was designed to work as Photonic Band Gap (PBG) structure. The PBG is a kind of structure that has a forbidden band for the certain range of frequencies and does not allow these forbidden frequencies to pass through them [38]. The PBG at the top was intended in the design to block an absorption of a range of incident photons but also intended to disallow the same range of photons' emissions. The authors through the design claimed that the PBG placed at the top would reduce the spectrum available for absorption but at the same time through stopping the emission out of the SC, one could achieve higher *Voc* without effecting the *Isc* from the SC. The design increases the overall PCE as the minority carriers' density available for absorption increases. The PBG influence can be more effective for designs using direct band gap materials, such as GaAs. In direct band gap materials, radiative recombination dominates and photons can be recycled after it is released due to radiative recombination and can be reused. In such cases, because of PBG structure at top, the recycled photon will not be allowed to direct out of the SC and would be available for absorption again within the SC.

Bozzola et al. in [36] and Zannoto et al. in [37] also demonstrated Si-SC designs with PNS-based LMS at the top surface facing the incident light, as shown in **Figure 5**. However, in contrast to Munday, they have used PNS as the diffraction grating to maximize the coupling of the incident solar spectrum to the AL through reduction in reflection and creating gradual refractive index variations. For PNS-based diffraction grating designs, it is required that the plane of periodicity must be perpendicular to the incident light. The design, instead of targeting or filtering only a range of wavelengths, has to work for the entire solar spectrum, and thus, needs to be carefully optimized.

In some other studies, the researchers have also demonstrated the designs for the PNS-based diffraction gratings at the top for different materials such as GaAs [9], InGaN/GaN [18] active materials. The results in all the cases, irrespective of the materials used have shown that these PNS have immense potential for taking the performance of the SC to new heights.

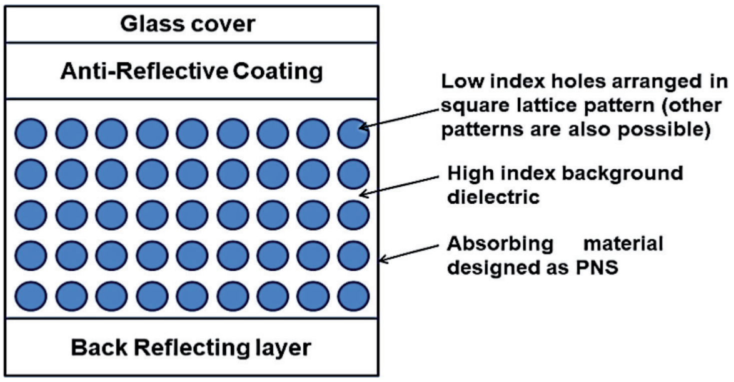

Figure 4.
Schematic design of a SC using PNS as absorbing layer.

In the article presented by Demesy et al. [46], it was discussed that it is possible to achieve PCE in the range of 15–20% just with 1 μm of Si active layer, if they are designed in the form of modulated nanowires. With careful optimization of the modulation profile, one can achieve significant enhancement in antireflection property, better light management, and back reflections of high wavelength photons simultaneously over broad angles. In this context, it is really interesting to find the structures that can use two different kinds of PNS structures together in the SC designs such as PhC and nanowires, as shown in **Figure 6**.

In another important study, Mallick et.al [47] also referred that for materials having indirect band gap and low absorption coefficient near the band edge, LMS are of utmost importance for the applications of SC. They have performed the analysis on the 400 nm thick Si AL-based SC. They have optimized the PNS through tuning of coupling photons of particular wavelengths to quasi-guided modes over a broad spectral range. The structure consists of two layers of PNS with different dimensions. The upper layer has a smaller radius of holes as compared to beneath layer. Their analysis has shown that there is a possibility of 8-fold increase in the average photon absorption compared to the planar SC with AL of same volume.

In another work, Eyderman et al. in [48] performed the study of the PNS effect on highly absorbing structures such as GaAs. They have used a slanted conical pore PNS packaged with SiO_2 and deposited on a silver back-reflector for their SC. They have performed the studies with ultra-thin GaAs layers from 100 to 300 nm and demonstrated that it is possible to tap almost 90% of the incident photons in the high wavelength range of 400–860 nm and achieved short circuit current density over 26.3 mA cm^{-2}. The quantitative analysis was further by Gupta et.al in [13] and provided the insight into the importance of the use of PNS-LMS for GaAs, including its effectiveness to improve the angular performance of the device.

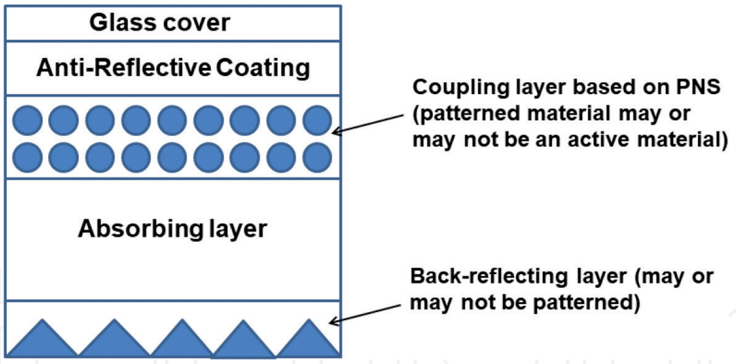

Figure 5.
Schematic design of a SC using PNS at the top for effective coupling of incident light. ARC can also be carved out as PNS structure.

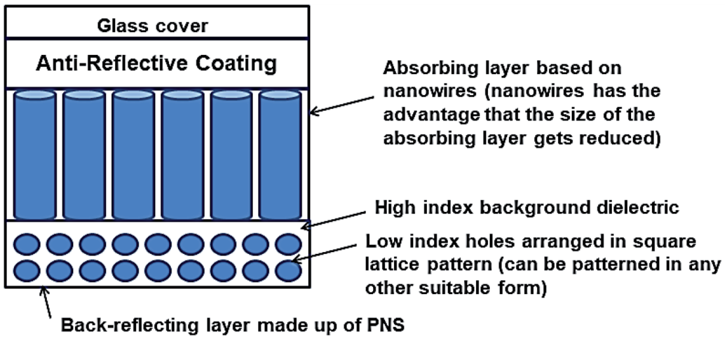

Figure 6.
Schematic design of a SC using nanowires as active structure in combination with PNS-based BR structure.

In one of the recent studies, Peer et al. in [49] has demonstrated theoretically that microlens arrays-based LMS can effectively enhance PCE of perovskite SC, and experimentally showed that the micro-lens can enhance organic SC efficiency. They have fabricated microlenses through nanoimprint lithography at the top surface and thus the design did not impact the material quality of the inside layers. Microlens pitch values near 1 micron were studied and PCE gains of 6% for thick perovskites SC were shown. The gains for thinner AL SC are expected to be larger, and it is conceivable that larger pitch values of several microns may provide better efficiency enhancement.

Bhattacharya et al. [50] and Hseih et al. [51] in their breakthrough research demonstrated that it is even possible to achieve PCE well beyond the Lambertian limits [25, 36] using PNS-LMS. They have demonstrated both theoretically as well as experimentally that using inverted pyramid and Teepee PNS it is possible with Si to surpass the limiting values. The inverted pyramid structure is recreated in **Figure 7**. They claimed that the main reason for overcoming the Si-SC limiting values using around 10–15-μm thick Si active layers are the existence of long lifetime, slow-light resonances, parallel-to-interface refraction and their coupling with external plane waves. These phenomena are not possible to be predicted using ray-optics models. They have demonstrated absorption beyond the limits in the weakly absorbing region of Si, near infrared wavelength range from 950 to 1200 nm. They achieved short circuit current density well beyond 41 mA/cm2. The study can pave the path for future studies related to PNS-based LMS and can have a long-lasting impact.

Till now, we have discussed about the role of PNS-based LMS for the single junction SC. However, it has also been shown that LMS also has a significant role to play for tandem SC designs. In the tandem cells, there are usually two cells (top and bottom) that are series connected electrically and hence it is required that these cells must be current matched. In the adverse case, the device output is limited by the smaller of the two cells' current and thus put the limit on the current of the entire tandem cell. To achieve optimized output, it is thus needed to optimize the thicknesses of each cell to get maximized PCE [52]. In such cases, usually LMS is critical to enhance the current out of the cell having lower current output.

In this regard, Mutitu et al. in [53] demonstrated a PNS-LMS that can be applied to both single junction and tandem cells. The 1D PNS structures are used as band-pass filters at the interface of two cells to reflect low wavelength photons (400–1100 nm) toward the top cell and transmit high wavelength photons. In addition,

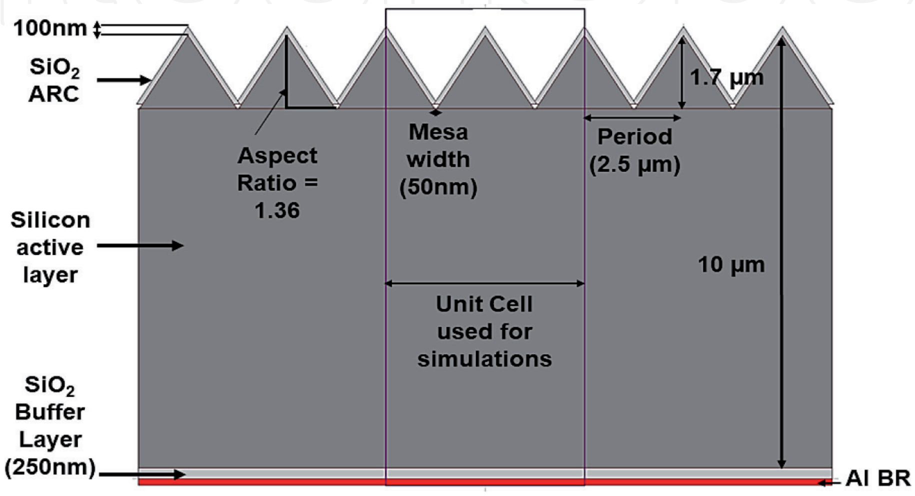

Figure 7.
The schematic diagram of the structure proposed in [51].

nanostructured diffractive gratings were incorporated to redirect incoming waves and hence increase the optical path length of light within the solar cells, and in turn, this has shown significant advancement in the PCE. In another well thought study, the researchers has highlighted the importance of PNS-LMS as intermediate reflectors for tandem cells [52], as shown in **Figure 8**, and achieved significant improvement in the output of the proposed design as compared to planar reflectors.

In the recent past, there is significant development has been done in tandem cells designs using perovskite/Si materials, where higher bandgap perovskite materials are used as the top cell and lower bandgap Si is used as bottom cell to take the final PCE routinely well beyond 30% [54, 55]. Several studies have been proposed in this regard including [56, 57], which have effectively demonstrated the role of PNS-based LMS with perovskite/Si materials tandem SC and help to establish the fact that LMS are also critical for the design of tandem cells irrespective of material system used.

All the abovementioned works, including others not mentioned here due to space limitations, have gradually helped to excavate the insights of the role that PNS-based LMS can play for the SC devices, especially for thin film SC. However, there still lies the challenges and whenever there is a challenge, lies an opportunity. The next section will discuss that in detail regarding the opportunities that are available for the future advancement to make these devices widely acknowledged and adapt more toward designing large area SC.

3.2 Light management for photoelectrochemical cells using periodic nanophotonic structures

PNS-based LMSs have shown above expectation utility for different optoelectronic applications, as already mentioned, and their effectiveness for SC application has already been discussed, and it is apparent to expect an enhanced performance from their adaptation for PEC photo-electrode designs. Various PNS-based LMSs have been studied for designing photo-electrodes, to be used for hydrogen production through water splitting, including, quantum wells [58], photonic crystals [59], quantum dots [60], carbon nanotubes [61], nanowires [62], etc. These PNS-based LMSs have, by one or other, shown their effectiveness for enhancing the photocatalytic activity through enhancing the absorption of incident photons and certainly led to increase in PCE for PECs.

Most of the efforts for PEC photo-electrode designs using PNS-based LMS are intended to modulate the band gap of the structure and take it near to 550 nm to utilize the maximum of the incident photons that have the capability of performing

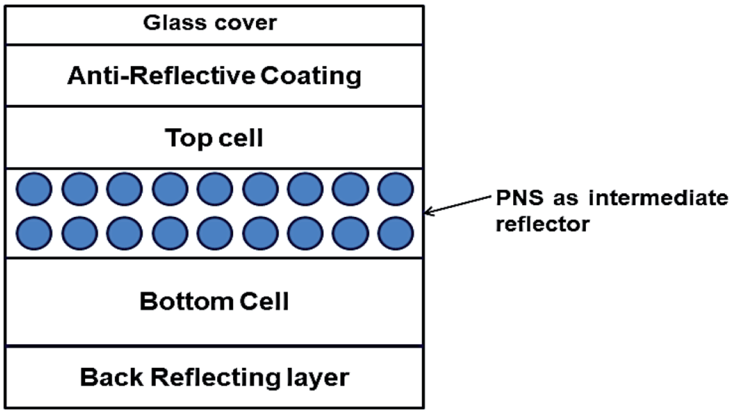

Figure 8.
The schematic diagram of the tandem SC with PNS-based LMS used as intermediate reflector.

photocatalytic action. In this regard, the PEC designs, especially, with nanowires are widely popular and researched. In one of such studies shown by Wang et.al [63], the GaN nanowires were designed using molecular beam epitaxy (MBE) process for wafer-level water splitting. Another highlight of the study was the observation of the stable operation of the PEC system emphasized that the PNS-based photo-electrode design based processes are equally stable in the aqueous solution. Thus, the design can serve the purpose of achieving absorption of the incident photons over the wider spectrum for enhanced photocatalytic operation with stable operation. Such early studies, including [64, 65], have also established the fact that Group-III nitride materials could be a better choice for photo-anode activity for oxygen evolution reaction.

Another study using PNS with Group-III material in [66] has shown that nonpolar GaN could lead to spontaneous water-splitting action together with enhanced proton diffusion process that can be achieved at low energy barrier. Although, the study demonstrated several important aspects of PNS-based PEC operations including achieving demonstration of better stability of GaN-PNS design as compared to TiO2 or ZnO-based design [67], the PCE achieved was still well under the acceptable 10%. The main reason was posed by the bandgap of GaN materials and its absorption coefficient [27, 68]. In another study, the GaN structure designed as nanowire is defect engineered with Mg impurity using epitaxial growth process [69]. In another research, Park et al. in [70], designed metal-assisted GaN nanowires with vapor-liquid-solid process and has done the growth over the graphene film. The structure was then transferred to polymer substrate to create a flexible PEC system. In contrast to GaN, $In_xGa_{1-x}N$ materials, during the past few years have established itself as a better prospect for designing photo-electrode for PECs due to the possibility of better band management with it and thus with PNS they are better positioned theoretically to tap the maximum possible solar irradiation [70, 71].

Kibria et al. were demonstrated the pioneering work on the multiband nanophotonic structures using $In_xGa_{1-x}N$/GaN materials [72]. The design is something kind of a tandem structure designed through carefully controlling the In concentration to do band engineering during the nanostructures growth. They observed the stable PEC operation of the structure till 560 nm, but still the output PCE was limited to 2% only due to the lattice mismatch arises due to the growth of $In_xGa_{1-x}N$ over the unmatched substrate. The researchers tried to further the performance of $In_xGa_{1-x}N$-based PEC operations through the use of light sensitive dyes with nanostructured photo-electrode designs [73, 74], however, the uncontrolled behavior of the space charge properties adversely limited the redox reactions and certainly restricts the PCE.

To improve the carrier extraction process, researchers have observed that controlling the band bending process in nanostructured $In_xGa_{1-x}N$ photo-electrode design and optimizing it is of utmost importance. Such a design has shown a considerable absorption improvement in the PEC process as compared to undoped samples, especially in UV and violet spectrum region [75]. In another study, Alvi et al. achieved In incorporation beyond 40% in the design of nanostructured $In_xGa_{1-x}N$ using PAMBE method and achieved notable enhancement in photocatalytic activity [76]. Caccamo et al. also demonstrated the improved water splitting activity through single crystal $In_{0.3}Ga_{0.7}N$/GaN core-shell type nanowires designed using MOVPE method [77]. In another interesting case, researchers observed experimentally that $In_xGa_{1-x}N$/GaN materials' photo-electrode designed as coaxial multi-quantum well nanowires for PEC operation significantly achieved absorption enhancement and demonstrated final PCE of 8.6% [78]. In one of the important studies, it has been shown that photocatalytic action can also be improved through a core-shell nanostructure-based photo-electrode designed with the combination of Si with $In_xGa_{1-x}N$ as compared to $In_xGa_{1-x}N$ nanostructures grown on Si substrate [79]. Although, inherently, due to lattice mismatch, growing $In_xGa_{1-x}N$ with Si, obviously increases the defects, the use of Si substrate or Si core can offer a benefit from economic perspective, thus need to be explored further.

To further the PCE for the hydrogen production through PEC process, multi-junction photo-electrode designs were also employed as demonstrated by Young et.al [80]. Their tandem structure was designed using GaInP/GaInAs materials in such a way that each junction bandgap could be independently varied. The design has shown a realistic potential to further the PCE and seems to be an exciting perspective. In another recent study, researchers in [81] have achieved the PCE of 8.75% with nanopatterned multiband $In_xGa_{1-x}N$/GaN-based photo-electrode design for one-step pure water splitting system. It has been highlighted in some other studies that for protection of the nanopatterned Group-III nitride photo-electrodes against photo-corrosion and surface oxidation, it is required to make their surfaces nitrogen rich, which ultimately leads to the longer operational life time for these PEC systems [82, 83].

In contrast to nanowire-based designs, Steiner et al. [58] presented the PEC design using quantum well-based LMS with superior strain management for the GaInP/GaAs photo-anode-based tandem PEC device. They highlighted that with tandem structure supported by PNS-based LMS, it is realistic to achieve PCE for PEC beyond the magical 10% value. For semiconductor photo electrode device constructed with quantum wells that can remain stick on the growth substrate, the authors claimed that the proposed configuration can also improve the stability of the system. Still, for such a design, the most challenging issue is to maintain critical strain balance and to reproduce such a structure with the equally desirable strain management must be carefully addressed. The factor ultimately put restriction to further increase the thickness of the active layer and limits the output and one possible way to improve the output further, again, is the better LMS.

In another exciting study, researchers in [59] observed the improved photocatalytic activity using PNS-based LMS accounted due to the enhanced absorption of incident photons near to the band edge of absorption material. They have designed the PNS using titania inverse opal topology. The photocatalytic materials used for photo-electrode was developed using nanoparticles of CeO2, ZrO2, and Y2O3. They observed that the PNS design's period has to be carefully optimized to enhance the absorption of the incident photons for the targeted wavelength range. Researchers in [60] have used a SnO2/TiO2 materials heterojunction photo-anode with quantum dots design. The study highlighted that with quantum dots-based heterostructure in place, enhanced electron transfer characteristics would be achieved as compared to the bare TiO2 photo-electrode.

In one of the recent studies, Alvi et al. stated to achieve highest PCE for single junction $In_xGa_{1-x}N$/GaN photo-electrode-based PEC system [7]. The photo-electrode design was accomplished with the combination of InN quantum dots on $In_xGa_{1-x}N$ nanowire. The output observed was claimed to be 2.5 times better for PCE and hydrogen generation as compared to the case with only $In_xGa_{1-x}N$ nanowires photo-electrode and the actual output achieved for this unassisted water splitting was 9.3%. The superior output was credited to the nanostructured $In_xGa_{1-x}N$ surface morphology optimization and enhanced electronic properties with quantum dots. On the adverse side, the design and growth process still is a complex issue and required to be simplified with further efforts.

The discussion has given a glimpse of the larger perspective of the research and designs that are achieved for the photo-electrodes LMS for PEC systems. The gradual improvement in the design and growth process has lifted the PCE for the

PEC systems from 0.1% to just under 10% for single junction and just under 20% for complex tandem photo-electrode designs. However, there is still a lot is required to be achieved for the wider acceptance of the PEC by taking their CE ratio to the suitable limits. Main challenge in this regard is posed by the fabrication and growth processes and if, one can solve the design issues, the PEC has an enormous potential to solve the sustainable electrical energy generation and storage issues.

4. Present challenges and future perspective

An optimized PNS-based LMS for OSEH applications has established the fact through several researches that they have massive potential to overcome the inherently restricted absorption of the incident solar spectrum photons in the limited thickness of the active layer to generate useful current. It has been shown that with these PNS-based LMS, it is even possible to surpass fundamental limits now [51], as discussed. Although, the study has shown for SC applications that the overall results for PCE is beyond limiting values, the beyond limit absorption in the particular case was observed for only higher wavelength photons, whereas for lower wavelength region, it was still under the Lambertian values and thus there is still room available for further improvement. The further improvement can be achieved with reducing reflection losses and losses due to recombination within the structure over the largest possible incident wavelength range and ultimately enhancing the coupling of incident light in the entire wavelength range, to the active layer, to convert them into useful absorption.

But, the main restraint with these PNS-based devices is posed by the growth and fabrication schemes. Repeatedly designing such a structure requires sophisticated infrastructure that is very capital intensive, which is the basic hurdle in achieving the low CE ratio with these devices. There are basically two approaches are being used for the realization of PNS, namely, top-down and bottom-up approaches.

Most of the PNS are designed with top down approaches that include nanofabrication tools such as electron beam lithography, focused ion beam lithography, dip-pen lithography etc. These top-down lithography processes commonly used for designing PNS have the ability to achieve high precision in nm range. But these processes are usually very time consuming and it is really difficult to adapt the process for large area commercial applications. Also, although the processes are precise, they more or less are very time consuming, expensive, mostly machine dependent, having low throughput and it is really difficult to adapt the process for large area commercial applications. These factors put the major restriction in the commercialization of the PNS-based OSEH designs.

On the other hand, some of the nanostructures such as nanowires are mostly grown through so called bottom-up approaches. The process has a major advantage that with it one can achieve bulk production and high throughput at low cost. Various tools such as chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), etc. are basically employed for these purposes [84] and growth is normally done in the presence of foreign catalysts. Although, the method is cost-effective and can provide bulk production at no time, it lacks precision and the process itself is mostly complicated. It is difficult to repeat the processes with same precision and many a times, even nonuniform and random profiles are achieved, even when one intends to generate periodic design. It is difficult to achieve the uniformity of the structure throughout the surface. The complex designs are really difficult to achieve with bottom-up approaches in the repeated manner.

As both top-down and bottom-up approaches has some limitations, one has to look toward a process that can have advantages of both. In this regard, during the recent years, several new techniques have rapidly came up to the arena due to their unique advantages including nanoimprint lithography [49], nanosphere lithography [85, 86], and self-assembled nano-masking scheme [87]. The processes promise to have all the major advantages related to top-down (due to the action of patterning the structured layers such as in a conventional lithography technique) and bottom up (due to the self-organization of the colloidal spheres) approaches and thus, are considered as viable inexpensive fabrication tools for producing regular and homogenous arrays of nanostructures with different sizes and need to be explored further.

An exciting scheme for OSEH for electrical energy generation that also deserves a special mention and seems very promising is the coupling of PEC with the conventional SC to electrolysis systems that can certainly improve the overall system's performance [21, 88]. The system can work for all day long operation and can be utilized to get electrical energy output during non-sunshine hours through electrochemical cells. Such a system can effectively developed as an alternate for the commonly used conventional SC and battery system and that too with better CE ratio, if designed with high PCE-based devices. The PCE of such a coupled system has been steadily improving [89, 90], and the indoor efficiency has already achieved the 30% mark [91]. However, the outdoor PCE is still limited, which is the foremost requirement for practical and commercial operations. Recently, Ota et al. [92] observed the record full day incident spectrum to the hydrogen conversion PCE of 18.78% for 470-W system under outdoor operation. It has been observed that to make this coupled system ready for the commercial and practical operations, it is primarily required to increase the involved individual components efficiency. The system, if optimized carefully, has a realistic potential to be considered for designing a reliable stand-alone system for future remote area lighting process as the overall set up will not be very heavy, and thus, the research efforts are required to be further in the area.

5. Conclusion

The chapter has discussed in details the technical perspective, advancements, requirement, and future trends for the PNS for designing the LMS for the solar energy harvesting applications that include solar cells and photoelectrochemical cells. The chapter put emphasis on the physical insight of the several engineered PNS designs that are being used for the purpose of LMS and how one can optimize the PNS for designing LMS. The chapter also discussed various bottlenecks that are still restricting the performance of the solar-to-electrical conversion process and highlighted several exciting methods for the further improvement in the performance of the device designs, which include utilizing tandem structures, improving the incident photons absorption through efficient spectrum harnessing using novel PNS, surface passivation processes, etc. From the discussion presented, one can appreciate the contribution that PNS-based LMS has made in the advancement of the SC and PEC devices and realize that it is due to the realistic potential of the PNS-based LMS that they have come down a long way, from merely a possibility to reality, to play a key role in achieving low CE systems for solar energy harvesting for sustainable development.

Conflict of interest

The author declares that there is no conflict of interest—whatsoever—related to financial or nonfinancial matters related to the work presented in the chapter.

Author details

Nikhil Deep Gupta
Centre for VLSI and Nanotechnology, Visvesvaraya National Institute of Technology, Nagpur, India

*Address all correspondence to: nikhildeepgupta@cvn.vnit.ac.in

References

[1] Brown K. United Nations Foundations [Online]. 2020. Available from: https://unfoundation.org/blog/post/5-global-issues-to-watch-in-2020/

[2] Ministry of New and Renewable Energy. Jawaharlal Nehru National Solar Mission: Towards Building SOLAR INDIA. New Delhi, India: Government of India; 2008

[3] NCPRE. Why Solar for Beginners [Online]. 2013. Available from: http://www.ncpre.iitb.ac.in

[4] Nelson J. The Physics of Solar Cell London. London, UK: Imperial College Press; 2008

[5] Green MA, Dunlop ED, Hohl-Ebinger J, Yoshita M, Kopidakis N, HA W. Solar cell efficiency tables (version 55). Progress in Photovoltaics. 2020;**28**(1):3-15

[6] Shockley W, Queisser HJ. Detailed balance limit of p-n junction solar cells. Journal of Applied Physics. 1961;**32**(510):510

[7] Alvi NH, Rodriguez PEDS, Hassan W, Zhou G, Willander M, Notzel R. Unassisted water splitting with 9.3% efficiency by a single quantum nanostructure photoelectrode. International Journal of Hydrogen Energy. 2019;**44**:19650-19657

[8] Naqvi A, Haug FJ, Soderstrom K, Battaglia C, Paeder V, Scharf T, et al. Angular behavior of the absorption limit in thin film silicon solar cells. Progress in Photovoltaics: Research and Applications. 2014;**22**(11):1147-1158

[9] Gupta ND, Janyani V. Design and analysis of light trapping in thin film GaAs solar cells using 2-D photonic crystal structures at front surface. IEEE Journal of Quantum Electronics. 2017;**53**(2):4800109

[10] Schuster CS, Bozzola A, Andreani LC, Krauss TF. How to assess light trapping structures versus a Lambertian Scatterer for solar cells? Optics Express. 2014;**22**(S2):A542-A551

[11] Green MA. Lambertian light trapping in textured solar cells and light-emitting diodes: Analytical solutions. Progress in Photovoltaics: Research and Applications. 2002;**10**:235-241

[12] Feng NN, Zhou GR, Huang WP. Space mapping technique for design optimization of antireflection coatings for photonic devices. Journal of Lightwave Technology. 2003;**21**(1):281-285

[13] Gupta ND, Janyani V. Lambertian and photonic light trapping analysis with thickness for GaAs solar cells based on 2D periodic pattern. IET Optoelectronics. 2017;**11**(5):217-224

[14] Zhou D, Biswas R. Photonic crystals enhanced light trapping in thin film solar cells. Journal of Applied Physics. 2008;**103**:093102

[15] Gupta ND, Janyani V. Design and optimization of photonic crystal diffraction grating based efficient light trapping structure for GaAs thin film solar cell. Journal of Nanoelectronics and Optoelectronics. 2016;**11**(4):407-415

[16] Davydov VY, Klochikhin AA, Seisyan RP, Emtsev VV, Ivanov SV, Bechstedt F, et al. Absorption and emission of hexagonal InN evidence of narrow fundamental band gap. Physica Status Solidi B: Basic Solid State Physics. 2002;**229**(3):R1-R3

[17] Wu J, Walukiewicz W, Yu KM, Ager JW III, Haller EE, Lu H, et al. Unusual properties of the fundamental band gap of InN. Applied Physics Letters. 2002;**80**(21):3967-3969

[18] Gupta ND, Janyani V, Mathew M, Maun M, Singh R. Design and fabrication of InGaN/GaN Superlattice based solar cell using photonic crystal structure at the front surface. Journal of Nanophotonics. 2018;**12**(4):043505

[19] Benton J, Bai J, Wang T. Enhancement in solar hydrogen generation efficiency using a GaN-based nanorod structure. Applied Physics Letters. 2013;**102**:173905

[20] Cai XM, Zeng SW, Zhang BP. Fabrication and characterization of InGaN p-i-n homojunction solar cell. Applied Physics Letters. 2009;**95**

[21] Sugiyama M, Fujii K, Nakamura S. Solar to Chemical Energy Conversion—Theory and Application. Tokyo: Springer; 2016

[22] Lobanova AV, Kolesnikova AL, Romanov AE, Karpov SY, Rudinsky ME, Yakovlev EV. Mechanism of stress relaxation in (0001) InGaN/GaN via formation of V-shaped dislocation half-loops. Applied Physics Letters. 2013;**103**(15):152106

[23] Nakamura S, Pearton S, Fasol G. The Blue Laser Diode. 2nd ed. Berlin: Springer-Verlag; 2000

[24] Yan B, Owens JM, Jiang C, Guha S. High-efficiency amorphous silicon alloy based solar cells and modules. MRS Symp Proc. 2005;**A23.3**:862

[25] Yablonovitch E, Cody GD. Intensity enhancement in textured optical sheets for solar cells. IEEE Transactions on Electron Devices. 1982;**29**(2):300-305

[26] Springer J, Poruba A, Mullerova L, Vanecek M, Rech O, K B. Absorption loss at nanorough silver back reflector of thin-film silicon solar cells. Journal of Applied Physics. 2004;**95**:1427-1429

[27] Zhao S, Nguyen HPT, Kibria MG, Mi Z. III-nitride nanowire optoelectronics. Progress in Quantum Electronics. 2015;**44**:14-68

[28] Gupta ND, Janyani V, Mathew M. Light trapping in p-i-n superlattice based InGaN/GaN solar cells using photonic crystals. Optical and Quantum Electronics. 2016;**48**(11):502, 1-517

[29] Gupta ND, Janyani V. Dense wavelength division demultiplexing using photonic crystal waveguides based on cavity resonance. Optik. 2014;**125**(19):5833-5836

[30] Paliwal A, Singh K, Mathew M. Effects of an undoped-InGaN waveguide on the optical confinement and carrier dynamics of InGaN laser diodes. Laser Physics. 2018;**28**(12):126204

[31] Leung SF, Zhang Q, Xiu F, Yu D, Ho JC, Li D, et al. Light management with nanostructures for optoelectronic devices. Journal of Physical Chemistry Letters. 2014;**5**(8):1479-1495

[32] Osterloh FE. Inorganic nanostructures for photoelectrochemical and photocatalytic water splitting. Chemical Society Reviews. 2013;**42**:2294-2320

[33] Chen X, Li C, Graetzel M, Kostecki R, Mao SS. Nanomaterials for renewable energy production and storage. Chemical Society Reviews. 2012;**41**:7909-7937

[34] Bermel P, Luo C, Zeng L, Kimerling LC, Joannopoulos JD. Improving thin-film crystalline silicon solar cell efficiencies with photonic crystals. Optics Express. 2007 Dec;**15**(25):16986-17000

[35] Feng N-N, Michel J, Zeng L, Liu J, Hong C-Y, Kimerling LC, et al. Design of highly efficient light-trapping structures for thin-film crystalline silicon solar cells. IEEE Transactions on Electron Devices. 2007;**54**(8):1926-1933

[36] Bozzola A, Liscidini M, Andreani LC. Photonic light-trapping versus Lambertian limits in thin film silicon solar cells with 1D and 2D periodic patterns. Optics Express. 2012;**20**(S2):224-243

[37] Zanotto S, Liscidini M, Andreani LC. Light trapping regimes in thin-film silicon solar cells with a photonic pattern. Optics Express. 2010;**18**(5):4260-4274

[38] Joannopoulos DJ. Photonic Crystals—Molding the Flow of Light. New Jersey: Princeton University Press; 1995

[39] Eyderman S, John S. Light-trapping and recycling for extraordinary power conversion in ultra-thin gallium-arsenide solar cells. Scientific Reports. June 2016;**6**(28303):1-7

[40] Ding H, Lalouat L, Gonzalez-Acevedo B, Orobtchouk R, Seassal C, Drouard E. Design rules for net absorption enhancement in pseudo-disordered photonic crystal for thin film solar cells. Optics Express. 2016;**24**(6):A650-A666

[41] Sheng X, Broderick LZ, Kimerling LC. Photonic crystal structures for light trapping in thin-film Si solar cells: Modeling, process and optimizations. Optics Communication. 2014;**314**:41-47

[42] Wang X, Khan MR, Gray JL, Alam MA, Lundstrom MS. Design of GaAs solar cells operating close to the Shockley–Queisser limit. IEEE Journal of Photovoltaics. 2013;**3**(2):737-744

[43] Chutinan A, Kherani NP, Zukotynski S. High-efficiency photonic crystal solar cell architecture. Optics Express. 2009;**17**(11):8871-8878

[44] Gupta ND. Absorption enhancement in hole Interface layer free perovskite solar cells using periodic photonic nanostructures. Optics and Laser Technology. 2019;**115**:20-31

[45] Munday JN. The effect of photonic bandgap materials on the Shockley-Queisser limit. Journal of Applied Physics. 2012;**112**:064501

[46] Demesy G, John S. Solar energy trapping with modulated silicon nanowire photonic crystals. Journal of Applied Physics. 2012;**112**:074326

[47] Mallick SB, Agrawal M, Peumans P. Optimal light trapping in ultra-thin photonic crystal crystalline silicon solar cells. Optics Express. 2010;**18**(6):5691

[48] Eyderman S, Deinega A, John S. Near perfect solar absorption in ultra-thin-film GaAs photonic crystals. Journal of Materials Chemistry A. 2014;**2**(3):761-769

[49] Peer A, Biswas R, Park JM, Shinar R, Shinar J. Light management in perovskite solar cells and organic LEDs with microlens arrays. Optics Express. 2017;**25**(9):10704

[50] SaJS B. Photonic crystal light trapping: Beyond 30% conversion efficiency for silicon photovoltaics. APL Photonics. 2020;**5**:020902

[51] Hsieh ML, Kaiser A, Bhattacharya S, John S, Lin SY. Experimental demonstration of broadband solar absorption beyond the Lambertian limit in certain thin silicon photonic crystals. Scientific Reports. 2020;**10**:11857

[52] Bielawny A, Rockstuhl C, Lederer F, Wehrspohn RB. Intermediate reflectors for enhanced top cell performance in photovoltaic thin-film tandem cells. Optics Express. 2009;**17**(10):8439-8446

[53] Mutitu JG, Shi S, Chen C, Creazzo T, Barnett A, Honsber C, et al. Thin film silicon solar cell design based on photonic crystal and diffractive

grating structures. Optics Express. 2008;**16**(19):15238

[54] Green MA. Commercial progress and challenges for photovoltaics. Nature Energy. 2016;**1**:15015

[55] Hossain MI, Qarony W, Ma S, Zeng L, Knipp D, Tsang Y. Perovskite/silicon tandem solar cells: From detailed balance limit calculations to photon management. Nano-Micro Letters. 2019;**11**:58

[56] Wang K, Jin Z, Liang L, Bian H, Bai D, Wang H, et al. All inorganic cesium lead iodide perovskite solar cells with stabilized efficiency beyond 15%. Nature Communications. 2018;**9**:4544

[57] Werner J, Nogay G, Sahli F, TCJ Y, Brauninger M, et al. Complex refractive indices of cesium—formamidinium-based mixed-halide perovskites with optical band gaps from 1.5 to 1.8 eV. ACS Energy Letters. 2018;**3**:742-747

[58] Steiner MA, Barraugh CD, Aldridge CW, Alvarez IB, Friedman DJ, Ekins-Daukes NJ, et al. Photoelectrochemical water splitting using strain-balanced multiple quantum well photovoltaic cells. Sustainable Energy & Fuels. 2019;**3**:2837-2844

[59] Rodrigueza I, Atienzar P, Ramiro-Manzano F, Meseguer F, Corma A, Garcia H. Photonic crystals for applications in photoelectrochemical processes: Photoelectrochemical solar cells with inverse opal topology. Photonics and Nanostructures. 2005;**2**(2-3):148-154

[60] Basu K, Zhang H, Zhao H, Bhattacharya S, Navarro-Pardo F, Datta PK, et al. Highly stable photoelectrochemical cells for hydrogen production using a SnO2–TiO2/quantum dot heterostructured photoanode. Nanoscale. 2018;**10**:15273-15284

[61] Dolmanan SB, Lai SC, Ke L, Loh WW, Jiao ZH, Sun XW. Improved photoelectrochemical cell with carbon nanotubes. IEEE Electron Device Letters. 2010;**31**(7):734-736

[62] Collazo R, Dietz N. The group III-nitride material class: From preparation to perspectives in photoelectrocatalysis. In: Photoelectrochemical Water Splitting: Issues and Perspectives. Cambridge, UK: RSC Publishing; 2013. pp. 193-222

[63] Wang D, Pierre A, Kibria MG, Cui K, Han X, Bevan KH, et al. Wafer-level Photocatalytic water splitting on GaN nanowire arrays grown by molecular beam Epitaxy. Nano Letters. 2011;**11**(6):2353-2357

[64] Maeda K, Teramura K, Saito N, Inoue Y, Domen K. Photocatalytic overall water splitting on gallium nitride powder. Bulletin of the Chemical Society of Japan. 2007;**80**(5):1004

[65] Kida TY, Minami Y, Guan G, Nagano M, Akiyama M, Yoshida A. Photocatalytic activity of gallium nitride for producing hydrogen from water under light irradiation. Journal of Materials Science. 2006;**41**:3527-3534

[66] Wang J, Pedroza LS, Poissier A, Fernández-Serra MV. Water dissociation at the GaN($10\bar{1}0$) surface: Structure, dynamics and surface acidity. Journal or Physical Chemistry C. 2012;**116**(27):14382-14389

[67] Jung HS, Hong YJ, Li Y, Cho J, Kim YJ, Yi GC. Photocatalysis using GaN nanowires. ACS Nano. 2008;**2**(4):637-642

[68] Zhang Z, Yates JT. Band bending in semiconductors: Chemical and physical consequences at surfaces and interfaces. Chemical Reviews. 2012;**112**(10):5520-5551

[69] Kibria MG, Chowdhury FA, Zhao S, Trudeau ML, Guo H, Mi Z. Defect-engineered GaN:Mg nanowire arrays for overall water splitting under

violet light. Applied Physics Letters. 2015;**106**:113105

[70] Wu J. When group-III nitrides go infrared: New properties and perspectives. Journal of Applied Physics. 2009;**106**:011101

[71] Benton J, Bai J, Wang T. Utilisation of GaN and InGaN/GaN with nanoporous structures for water splitting. Applied Physics Letters. 2014;**105**(22):2012-2017

[72] Kibria MG, Nguyen HPT, Cui K, Zhao S, Liu D, Guo H, et al. One-step overall water splitting under visible light using multiband InGaN/GaN nanowire heterostructures. ACS Nano. 2013;**7**(9):7886-7893

[73] Kibria M, Chowdhury F, Trudeau M, Guo H, Mi Z. Dye-sensitized InGaN nanowire arrays for efficient hydrogen production under visible light irradiation. Nanotechnology. 2015;**26**(28):285401

[74] Kibria MG, Zhao S, Chowdhury F, Wang Q, Nguyen HPT, Trudeau ML, et al. Tuning the surface Fermi level on p-type gallium nitride nanowires for. Nature Communications. 2014;**5**:1-6

[75] Chowdhury FA, Mi Z, Kibria MG, Trudeau ML. Group III-nitride nanowire structures for photocatalytic hydrogen evolution under visible light irradiation. Applied Physics Letters. 2015;**3**:104408

[76] Alvi NH, Soto Rodriguez PED, Kumar P, Gómez VJ, Aseev P, Alvi AH, et al. Photoelectrochemical water splitting and hydrogen generation by a spontaneously formed InGaN nanowall network. Applied Physics Letters. 2014;**104**:223104

[77] Caccamo L, Hartmann J, Fàbrega C, Estradé S, Lilienkamp G, Prades JD, et al. Band engineered epitaxial 3D GaN-InGaN core-shell rod arrays as an advanced photoanode for visible-light-driven water splitting. ACS Applied Materials & Interfaces. 2014;**6**(4):2235-2240

[78] Ebaid M, Kang JH, Lim SH, Ha JS, Lee JK, Cho YH, et al. Enhanced solar hydrogen generation of high density, high aspect ratio, coaxial InGaN/GaN multi-quantum well nanowires. Nano Energy. 2015;**12**:215-223

[79] Hwang YJ, Wu CH, Hahn C, Jeong HE, Yang P. Si/InGaN Core/shell hierarchical nanowire arrays and their photoelectrochemical properties. Nano Letters. 2012;**12**:1678-1682

[80] Young JL, Steiner MA, Döscher H, France RM, Turner JA, Deutsch TG. Direct solar-to-hydrogen conversion via inverted metamorphic multi-junction semiconductor architectures. Nature Energy. 2017;**2**:17028

[81] Chowdhury FA, Trudeau ML, Guo H, Mi Z. A photochemical diode artificial photosynthesis system for unassisted high efficiency overall pure water splitting. Nature Communications. 2018;**9**:1707

[82] Kharche N, Hybertsen MS, Muckerman JT. Computational investigation of structural and electronic properties of aqueous interfaces of GaN, ZnO, and a GaN/ZnO alloy. Physical Chemistry Chemical Physics. 2014;**16**:12057-12066

[83] Kibria MG, Qiao R, Yang W, Boukahil I, Kong X, Chowdhury FA, et al. Atomic-scale origin of long-term stability and high performance of p-GaN nanowire arrays for photocatalytic overall pure water splitting. Advanced Materials. 2016;**28**:8388-8397

[84] Zhao S, Le BH, Liu DP, Liu XD, Kibria MG, Szkopek T, et al. p-type InN nanowires. ACS Nano Letters. 2013;**13**(11):5509-5513

[85] Wu LY, Ross BM, Lee LP. Optical properties of the crescent-shaped

nanohole antenna. Nano Letters. 2009;**9**(5):1956-1961

[86] Zhang Q, Ghosh S, Samitsu S, Peng X, Ichinose I. Ultrathin freestanding nanoporous membranes prepared from polystyrene nanoparticles. Journal of Materials Chemistry. 2011;**21**(6):1684-1688

[87] Mathew M, Sodabanalu H, Sugiyama M, Nakano Y. Orange/yellow InGaN/AlN nanodisk light emitting diodes. Physica Status Solidi C: Current Topics in Solid State Physics. 2013;(11):1525

[88] Chu S, Li W, Yan Y, Hamann T, Shih I, Wang D, et al. Roadmap on solar water splitting: Current status and future prospects. Nano Futures. 2017;**1**: 022001:1-29

[89] Barbir F. PEM electrolysis for production of hydrogen from renewable energy sources. Solar Energy. 2005;**78**(5):661-669

[90] Ager JW, Shaner MR, Walczak KA, Sharp ID, Ardo S. Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. Energy & Environmental Science. 2015;**8**:2811-2824

[91] Jia J, Seitz LC, Benck JD, Huo Y, Chen Y, Ng JW, et al. Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30. Nature Communications. 2016;**7**:13237

[92] Ota Y, Yamashita D, Nakao H, Yonezawa Y, Nakashima Y, Ebe H, et al. Highly efficient 470 W solar-to-hydrogen conversion system based on concentrator photovoltaic modules with dynamic control of operating point. Applied Physics Express. 2018;**11**:077101