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Advances in nanostructured thin film materials for solar cell applications

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Abstract

This paper reviews recent advances in photovoltaic devices based on nanostructured materials and film designs, focusing on cadmium telluride (CdTe), copper zinc tin sulphide (CZTS), dye-sensitized solar cells (DSSCs) and perovskite solar cells. The current major challenges associated with the development of thin film solar cells are the reduction in manufacturing cost and increase in efficiency and performance. The CdTe and CZTS films have been investigated extensively due to its cheap and abundant elemental constituents and better physical properties. Solar cells based on the nanostructured technology including the DSSCs have also made wide impact into the solar cell industry in terms of manufacturing cost and improved efficiency. Perovskite solar cells have received significant interest recently due to its potential high efficiency.

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Table of Contents

1. Introduction

Due to the rapid growth of population and extensive usage of newly developed electricity-consuming devices, the energy consumption throughout the world is predicted to be increased at the rate of 1.5% per annum from 2010 to 2040 as shown in **Figure 1** [1-4], and it is estimated that 30 TW of energy is needed globally by the year 2050. This need will lead to a significantly increased energy demand from 16,999 to 42,655 Terawatt-hours (TWh) in the years from 2007 to 2050 respectively, with an annual increase rate of 2.0% [5]. The electricity demand in the non-Organization for Economic Co-operation and Development (non-OECD) countries grows by 3.1% a year, which is almost three times faster than that in the OECD countries [5]. More than ten million people from the developing countries will need to get access to electricity up to year 2050, and large amount of energy up to 36,948 TWh will be needed [6]. Renewable energy resources play a critical role in coping with this huge demand of energy consumption. Among these, solar cell energy is regarded as one of the best solutions, and the decrease in the manufacturing cost of the solar cell devices is boosting the solar energy market, which will be comparable with the other available renewable energy resources. The annual market share of the photovoltaic technologies from year 2000 to 2015 is shown in **Figure 2** and the growth rate for the photovoltaics (PV) industry is ~30% per annum in the last decade and is increasing consistently [7]. The PV modules have contributed considerable power to the market annually which is 61400 GW by the end of 2015 [8]
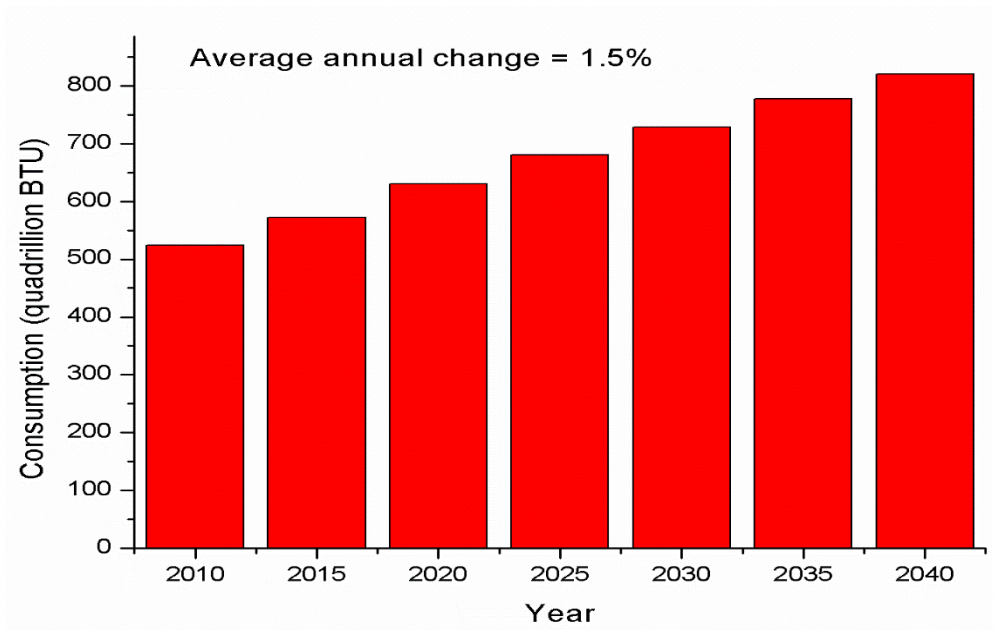
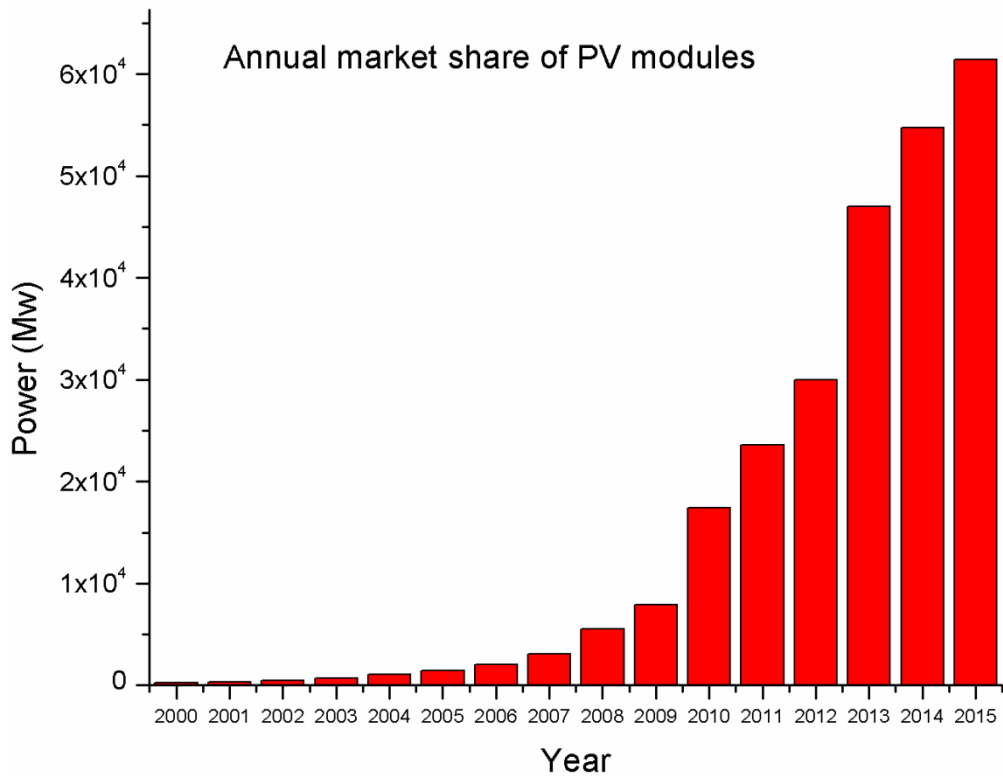**Figure 1.** World energy consumption, 2010-2040 (quadrillion BTU)

Figure 2. Annual market share of PV modules

Today 80 to 90% of the solar cell technology is dominated by silicon-based materials [9], and silicon technology is the main-stream and proven to be robust technology in the PV modules. The reason behind is that the silicon is the leading material used in bulk (1st generation), thin film (2nd generation) and some of the nano-structured (3rd generation) solar cells for photovoltaics. However, the highest efficiency for non-concentrated silicon solar cell design reported so far is 25% only [10]. It is difficult to further increase the efficiency, although following methods have been employed:

- Use of hydrogenated silicon [11]

- Use of nano particles as the back electrodes [12]

- Use of textured back surface reflector [13]

- Use of ZnO based back reflector in triple junction thin film solar cell [14]

- Use of concentrators on different substrates [15]

- Use of double and triple junctions [16]

- Incorporation of oxygen in Si, etc. [17]

- Nanostructured designs, such as p-n junction Si micro/nano-wire arrays and quantum dots [18], or nano-scale honeycomb structures [19].

There is also another concern about the high price of silicon wafers due to its extraction from the raw materials [20]. In order to reduce the cost and achieve high potential efficiency in the solar cells, it is critical to apply new materials with accompanying advantages such as abundant availability, less-toxicity, stability and growth with easy deposition techniques [21]. Generally, the recently extensively investigated solar cell materials include; thin films of CdTe, CZTS, SnSbS, CIGS, etc.; Dye-sensitized TiO_2 and ZnO and their nanostructures; composite material CuO/ZnO, CIS/TiO_2, etc., homojunction materials, such as Cu_2O; and perovskite based solar cells, etc. Figure 3 shows the efficiencies plot for the key materials published in the current review from 2010 onward (modified from NSL website). It can be inferred from the figure that the efficiency of the pervoskite solar cell increases significantly.
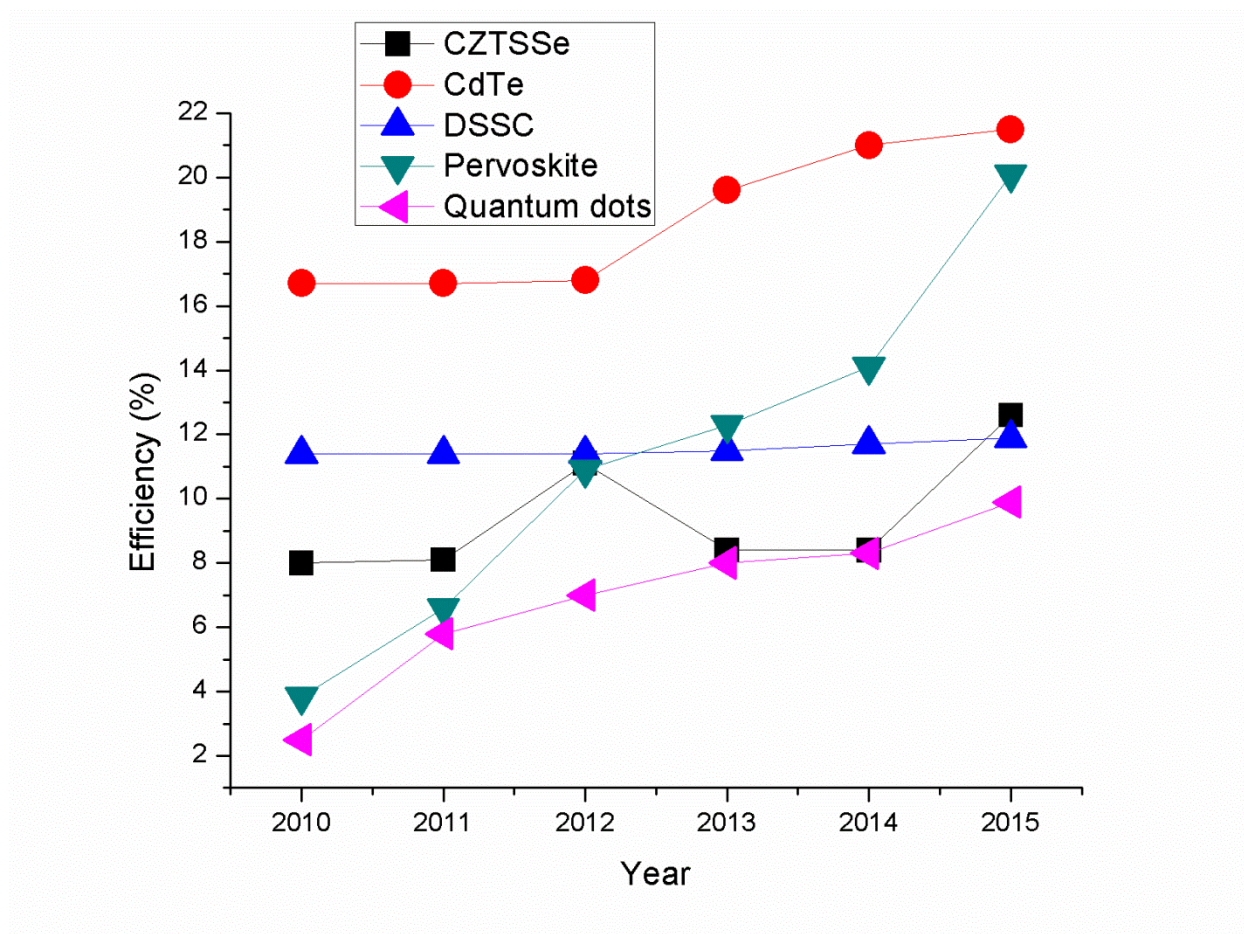
Figure 3. Solar cell efficiency chart (2010-2015) [22-26]

2. Hetero-junction thin film solar cells

2.1 CdTe thin films

The research on CdTe thin film solar cell started since 1950's, and the current research efforts are devoted for improving efficiency of the CdTe thin film solar cells. Since CdTe has an optimal band gap of 1.49 eV for single-junction devices, efficiencies above 20% should be achievable in the commercial CdTe solar cells [27]. For example, in August 2014, First Solar reported a device with 21.0% conversion efficiency [28]. The efficiency of the CdTe/CdS thin film solar cells was reported to be 22% [29]. However, the stability of efficiency could be a potential problem for the CdTe based solar cells due to existence of defects in grain boundaries and intra-grain dislocations. It is presumed that the carriers recombine, and reduce the average life time of minority carriers [30]. The photovoltaic performance of the CdTe solar cells depend not only on

efficiency but also on many other factors such as open circuit voltage V_{oc}, fill factor (FF), choice of substrate, close circuit current J_{sc} and area of deposition. The configuration of the solar cell also influences the performance of the solar cell for example, the superstrate solar cell has been applied in order to improve the absorption capability of the solar cell [31]. The maximum efficiency values of the laboratory and commercial scale, and the associated solar cell parameters with respect to different preparation methods are listed in **Table 1** [31-46]

Table 1. CdTe solar parameters fabricated with close space sublimation (CSS), vapor transport deposition (VTD) and high vacuum evaporaton (HVE) in substrate and superstrate configuration

Superstrate configuration (Laboratory scale)							
Method	Efficiency	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	Area	Substrate	Ref
CSS	19.6%	857	28.6	80.0	1.04	Glass	[47]
VTD	19%	*872*	28.0	78.0	0.48	Glass	[41]
VTD	16.4%	835	23.8	*82.5*	0.36	Glass	[42]
Substrate configuration (Laboratory scale)							
HVE	13.6%	852	21.2	75.3	0.3	Glass	[43]
Commercial technology							
VTD	16.1%	68.7	2.25	74.8	0.72	N/A	[48]

The values of V_{oc} and FF for the optimized deposition and fabrication technologies of the CdTe solar cells are around 1000 mV and 85% respectively. These optimized values of fill factor (FF) and open circuit voltage (V_{oc}) along with the short circuit current density (J_{sc}) ~27 mAcm^{-2}, can result in 21±0.5% efficient laboratory scale CdTe solar cell [48]. It is possible to increase V_{oc} by increasing the built-in voltage and maximizing the net acceptor density in the absorber region of the CdTe thin film materials. It was observed that a higher value of V_{oc} can be obtained by increasing the doping level (Cu dopant), but with the increase in V_{oc} the value of FF was reduced which affected the overall performance of the solar cell [48]. The increase in the acceptor density

will decrease the width of the space charge region. Effect of compensating acceptors was also observed due to the probability of Cu involvement into the window layer [49]. These effects cause the reduction in space charge width which increases the probability of light absorbance in the undepleted region [50].

Kim et al. [51] studied the environmental issues of CdTe thin film solar cell. Carbon emission from the CdTe device is 62.5% lower than a-Si PV system and 83.5% lower than a single crystal silicon photovoltaic panel [52]. For each gram of CO_2 emission in the energy production from the grid, 0.03 μg arsenic, 0.01 μg of cadmium, 0.09 μg of chromium, 0.1 μg of lead (Pb) and 0.01 μg of mercury (Hg) are emitted. Such emissions can be reduced 95-98% by using the CdTe based photovoltaic devices. Once the CdTe PV system is synthesized, it could be served as a durable and environmental friendly device for photovoltaics [53].

2.2　CdTe based Quantum dots solar cells

Nanotechnology and quantum dots (nano-sized semiconductor particle) have been introduced into solar cells in order to further increase their efficiency above the theoretical limit set by Shockley-Queisser thermodynamics [54]. The properties of quantum dots are size dependent with extraordinary tunable band gaps, high extinction coefficient, and most importantly multiple exciton generation [55]. It was reported that the the band gap of CdTe can be tuned to a desirable value by altering the size of the quantum dot to match the desired band gap range [56].

In a quantum dot solar cell, synthesized quantum dots are subjected to illumination for the generation of electron hole pair inside the quantum dots. The electrons from the exciton will enter into the conduction band of the quantum dot where it is captured by the conduction band of a wide band gap semiconductor (such as AlN, GaN and TiO_2) and percolates in the wide band gap network and eventually reaches the conducting glass (an example is shown in **Figure 4**). The electron travels through the load thus completing the circuit as it enters the device through back electrode. This electron after passing through different stages recombines with the hole left behind in the valance band of quantum dot and thus equilibrium is maintained [57]. Wang et al reported that multicrystalline Si solar cells with quantum dots are expected to have a maximum

efficiency of 77%.[58-59]. Further increase in the efficiency can be obtained from multiple exciton generation (MEG) from a single photon in a few materials such as PbS and PbSe [60]. The generation of multiple excitons has not been accomplished in the CdTe quantum dots. However, there are some latest investigations which revealed the generation of such multiple excitons [61]. The generation of multiple excitons is possible when many excitons are generated from a single photon upon impact ionization. The excess energy equals to the difference between photon energy and band gap, and this will provide a surplus temperature, which is higher than the lattice temperature [62].
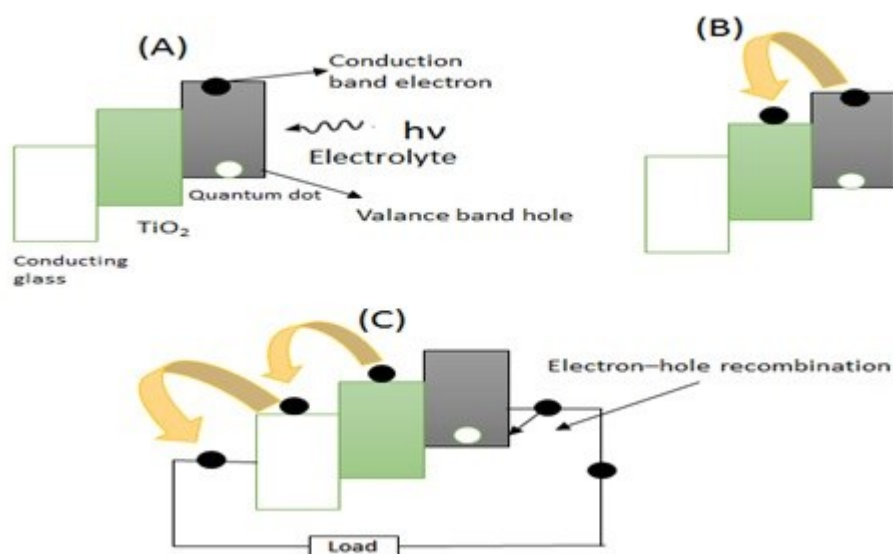
Figure 4. Quantum dot solar cell (A) the electron is excited into the conduction band; (B) electron enters into the conduction band of TiO_2; (C) electron-hole recombination after passing through electrolytic solution.

CdTe materials show a bit higher toxicity levels than many other materials used in photovoltaics, and its toxicity increases as the size of the particle decreases and therefore quantum dots of CdTe are found to be more toxic. Song et al. [63] compared the relative toxicity of gold (Au) and carbon (C) nano particles with CdTe nano particles based on its metabolic activity in living cells and plants growth, and indicated the relative toxicity in a sequence of CdTe quantum dots, to Au

nano particles, and then to carbon nano dots. Xiao et al. [64] studied the toxicity of cadmium like materials and found that CdTe is less toxic than Cd, based upon the damage of multiple cellular cites of mice prompted by the quantum dots. The issue of toxicity is of great importance and how to handle such materials during synthesis might be a million dollar question.

2.1 CZTS thin films

Similar to the CdTe, copper indium gallium selenide (CIGS) is one of the most investigated candidates among the second generation or thin film solar cells with a reported maximum efficiency of XX%.. However, there are some issues regarding to its cost of raw materials and toxicity. CZTS, with a kesterite structure, is considered to be an alternative material to the CIGS which is currently under extensively development. CZTS is assumed to be analogous to CIGS when Indium (III) is replaced by Zn (II), Ga (III) is replaced by Sn (IV) and Se (VI) by S (VI). The first principles calculation about crystal energy suggested that both the structures can co-exist as the crystal energy for stannite structure is only 2.86 meV per atom larger than that for the kesterite structure [65]. Optoelectronic and structural properties of both the CIGS and CZTS can be enhanced by replacing its constituent elements with earth abundant and nontoxic elements, such as $SnSbS_4$ and CuS, etc [66]. For the CZTS, the high absorption coefficient ($10^4 \, cm^{-1}$) and optimum band gap (1.0–1.5 eV) covers the maximum solar spectrum and opens a gateway for economic and ecological thin films device fabrication. The highest achieved efficiency (12.7%) was reported via hydrazine based non-vacuum particle solution approach, although the theoretical efficiency value is 32.4% [52,67].

CZTS has been synthesized using different techniques in the form of thin films and nano crystal quantum dots. The available techniques include thermal evaporation, hybrid sputtering, atomic beam sputtering, electron beam evaporation, pulsed laser deposition, photochemical deposition, iodine vapor transport method, one-pot synthesis of colloidal nanoparticles, a modified Bridgman technique, chemical vapor deposition, photochemical deposition, electroplating, spray pyrolysis, sulfurization of precursors and electrochemical route for deposition [68-69]. In the above stated techniques, electrochemical deposition method is a non-vacuum technique with a low cost and low temperature. However, the material utilization for such non-vacuum process is very high. The best method according to our literature survey for deposition of the uniform

CZTS thin films on a large scale is non-vacuum electro-deposition technique [70-71]. By optimizing the process parameters, the defects in the film can be reduced, which ultimately enhance the crystal quality as well as the performance of the device. Due to technological interest in the CZTS solar cells, the number of research publications (obtained from Elsevier) has been tremendously increased from 2000 to 2015 as shown in **Figure 5**.
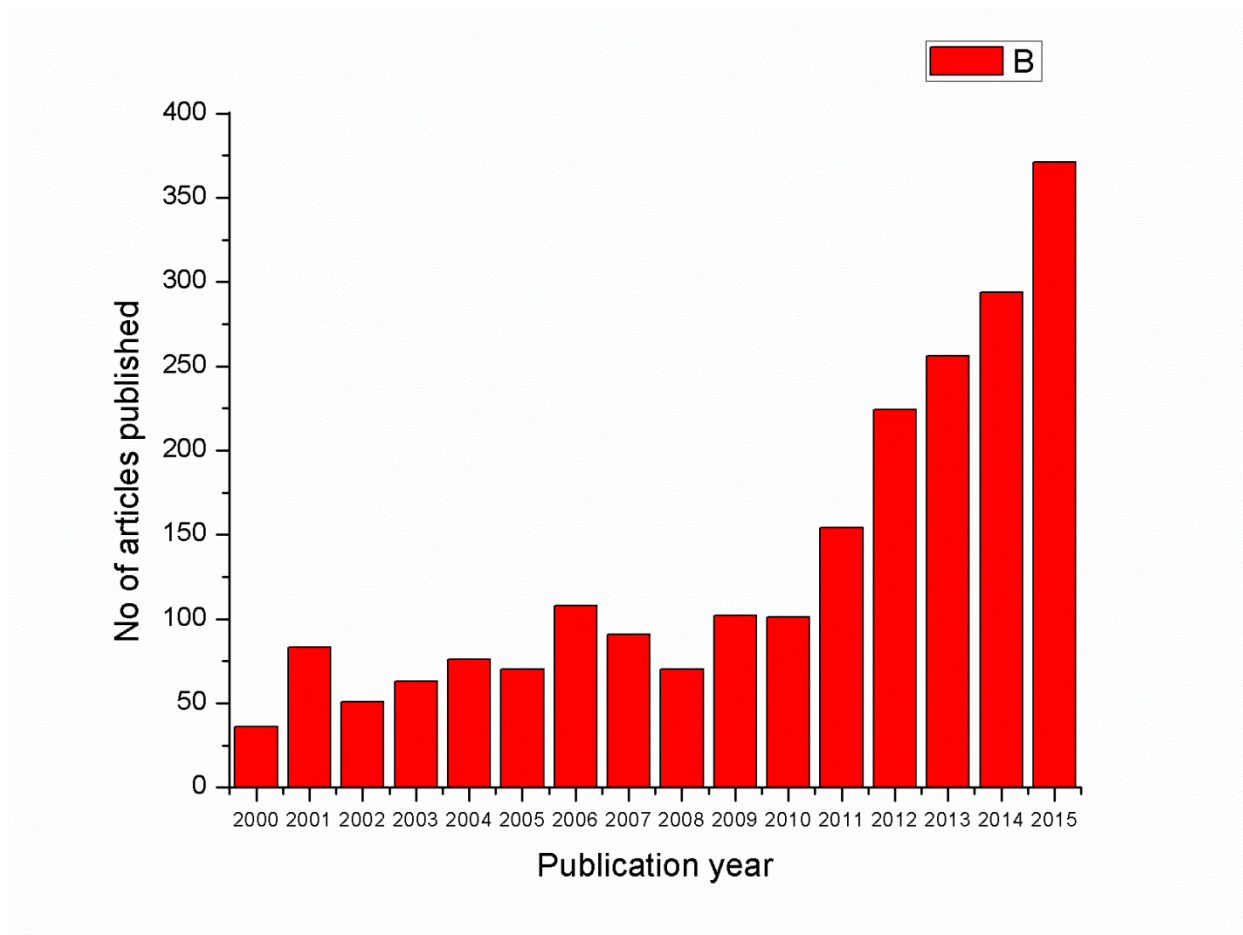

Figure 5. Publication chart for CZTS (obtained from Elsevier 2000-2015)
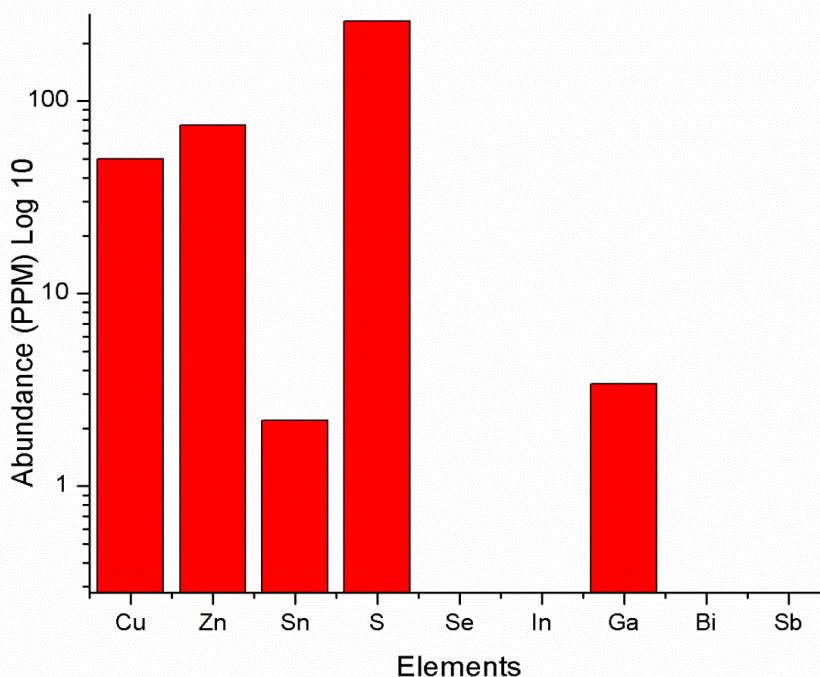
Figure 6. Abundance of different materials in earth crust [72-73]

The abundance of different elements in earth crust used in the CZTS and CIGS solar cell materials as compared to others is shown in **Figure 6**. Ga and In are the rare elements in the earth crust therefore their prices almost get doubled every year due to the market demand. The price comparison of a few key elements is shown in **Figure 7**, and clearly among them In, Ga and Se are the most expensive materials in use. Indium is used as an important element in the CIGS solar cell and the efficiency of the CIGS solar cell is highest (20.9%) in thin film technologies approaching to c-Si solar cells. Due to this reason, indium based cell (CIGS) are gradually dominating the solar energy market which is supposed to increase the manufacturing price of the photovoltaic modules. The scarcity of the materials is a consistent problem for the technology and there is no immediate solution for overcoming this issue. The reason is that cadmium (Cd) and In are the by-products of Zn refining while selenium (Se) and Te are the by-products of Cu refining. It means that these rare materials are subjected to the demand of Zn and Cu. The use of In in ITO as transparent conducting oxide (TCO) is also important to serve as front contact in photovoltaic devices. It is possible to replace the ITO by other TCOs such as Al

doped zinc oxide (AZO) or Al doped tin oxide (ATO). The price of the device has a negative impact on the future ambitions for developing a technology which can be subtly dependent on the social economic profile of PV market business. The reprocessing of old PV modules is reducing the demands of raw materials. It is therefore presumed that the PV modules should be replaced after usage for 20-30 years uses and can be recycled for recovering the materials for further usage [74-75].
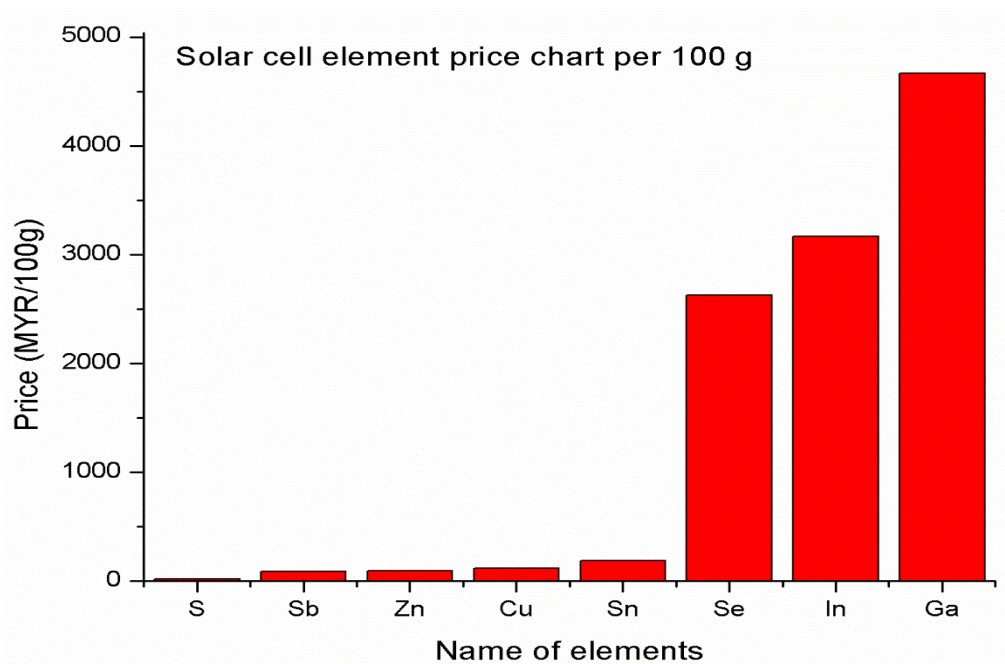
Figure 7. Price chart for solar cell materials [http://www.lesker.com]
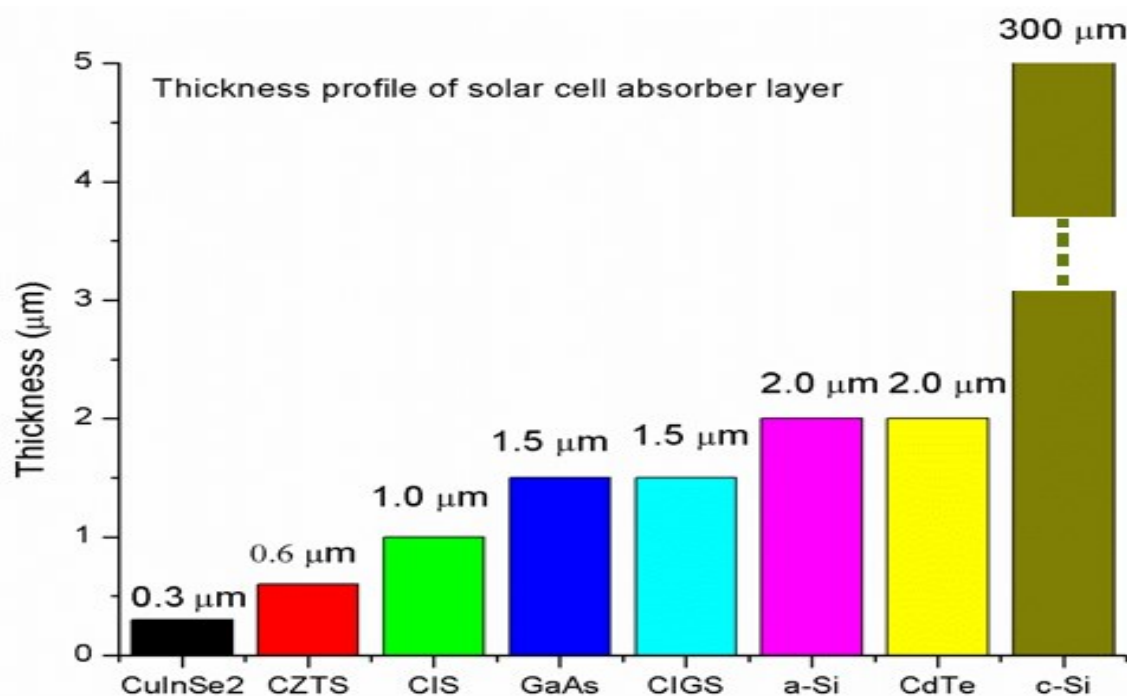
Figure 8. General thickness profile of absorber layer (for most solar cells)

The thickness of the CZTS thin films and other related materials is strongly related to the properties of thin films. It was observed that the fill factor and short circuit current density decreased with the increase in the film thickness [75]. The increase in the series resistance of the thicker layers of the fabricated thin film is responsible for the deterioration of the properties. The increase in the thickness of thin film with the substrate temperature [76] is related with the decrease in sticking coefficient as well as the increase in the density of the film due to crystallization. The absorber layers in PV technology are categorized according to their thickness represented in **Figure 8** [77-81]. The thinnest material used in thin film PV technology is CuInSe$_2$ while the thickest one is c-Si. However, CuInSe$_2$ due to its usage of rare elements is not the preferred material in solar cell technology.

2.2.3   Tin antimony sulphide thin films

Tin antimony sulphide (Sn-Sb-S), one of the sulfosalts, is also an emerging material and a possible replacement of the toxic and expensive materials, and has plenty of potential applications in photovoltaics and optoelectronic devices [61]. Tin antimony sulphide has different phases such as SnSb$_2$Se$_4$, Sn$_3$Sb$_2$S, Sn$_3$Sb$_2$S$_6$, Sb$_2$Sn$_5$S$_9$, SnSb$_2$S$_4$, Sn$_4$Sb$_6$S$_{13}$ and

Sn$_6$Sb$_{10}$S$_{21,}$ etc. [68]. Gassoumi and Kanzari [82] used the Sn-Sb-S as an absorber layer, and observed that the material possesses an n-type conductivity and a high resistivity with excellent absorption ability. The band gap value of the Sn-Sb-S thin films lies in the range of photovoltaic materials, and it can be tuned further to be more suitable for solar cell. Post annealing of the Sn-Sb-S thin films in an inert atmosphere was reported to reduce the voids and increase the grain size which further improves the electrical and optical properties. Abdelkader et al. [83] reported that the variation in the energy band gap of the Sn-Sb-S thin films is due to the variation in Sn content which changes the average coordination number. A high absorption coefficient (10^5 cm^{-1}) was reported for this emerging material with a high photoconductivity in visible and near infrared region [83]. The effect of oxygen annealing on the properties of Sn-Sb-S thin films was studied by Fadhli et al. [84]. They reported that the extra phases of SnO$_2$ appeared at a high annealing temperature and the incorporation of oxygen in Sn-Sb-S reduces the resistivity of the material due to paramagnetic nature of the oxygen, which increased the photoconductivity and optical properties of the obtained thin films [85]. Sn-Sb-S was reported to be an n-type material, and thus mostly p-type material is used as an absorber layer in the fabrication of solar cells. It was reported that at high (above 300°C) annealing temperature, the conductivity of Sn-Sb-S changed from n to p-type, therefore Sn-Sb-S has dual conductivity (p and n-type) [86].

3. Dye sensitized solar cells

Recently DSSCs have gained extensive attention because of their low production cost, ease of fabrication and tunable optical properties, such as color and transparency. The amendable aesthetic features (color and transparency), ease of fabrication and earth abundance of many compositional materials for the DSSCs are special properties for photovoltaic applications [87].

The main components of the DSSCs are dye sensitized photo anode, counter electrode and redox electrolyte. In photo-electrochemical systems, many semiconductor materials have been used as photoelectrodes, including single crystal and poly crystalline material of Si, InP, GaAs, CdS, etc. The efficiency of these materials with a suitable redox electrolyte is generally limited to 10%

under sunlight irradiation. The photo degradation of the electrolyte under irradiation reduces the life of the cell by destabilization. ZnO, TiO_2 and SnO_2 are wide band gap oxide semiconductor materials, and widely used as photo-electrodes in the DSSCs. After using photosensitizers, various inorganic/organic dyes can be adsorbed on the surface of photoanode , thus absorbing visible light [88]. Gong et al. [44] presented a review on the fundamental concept of DSSCs, and discussed the novel materials for DSSCs. They examined the basic working principle, recent developments and future prospects of the DSSCs technology. Effects of various parameters like sensitizer, semiconductor oxides, contacts, morphology, electrolyte and substrate etc. on the performance of DSSCs have been explained. It has been concluded that DSSCs are more sensitive to visible light than crystalline silicon, which made them as a reliable power source in low intensity environment like dawn and dusk and also the overall efficiency is not seriously affected by high temperature. With the continued research efforts DSSCs could become a reliable power provider in the future [46].

Li et al. [46] have given the basic principle solid state dye sensitized solar cells and discussed the different types of solid or quasi solid state hole conductors such as p-type semiconductors, ionic liquid electrolytes and polymer electrolytes. The solid state cells containing p-type semiconductors were considered to possess the advantage of easy fabrication and higher stability, whereas the DSSCs based on the polymer electrolytes showed the higher efficiency and wide future applications [46].

The methods to increase the efficiency of DSSCs include:
1. To develop new photosensitizers with a higher molar extinction coefficient.
2. To improve open-circuit voltage of DSSC. The open-circuit voltage is the difference between the quasi-Fermi levels of the electrons in semiconductor and the redox couple in electrolyte.
3. To reduce the losses in the solar cell caused by charge recombination, electron trapping, and optical reflection, etc.

3.1   TiO$_2$ films and nanostructures

TiO$_2$ is used as thin film solid state DSSCs (SS-DSSCs) and nanostructured DSSCs. In the thin films SS-DSSC, TiO$_2$ is normally deposited on conducting transparent glass as an electrode in the solar cell , generally using "doctor blading" method [89]. The dye molecules are attached to the surface of TiO$_2$ particles by a chemical bond, i.e., or generally called sensitization.   In nanostructured TiO$_2$ DSSCs (nano particles, nano wires, nanotubes, nano rods), TiO$_2$ provides a large surface area for dye molecule anchoring. The absorbed photons are split at the surface of the nanostructure and the band alignment of dye, and the photo-generated electrons are injected into TiO$_2$ and the hole is scavenged by redox species **(see Fig. 9).** The electrolyte solution (iodine or tri-iodide) is often used to neutralize the electron and hole after passing through the load [90].

SS-DSSCs show that their open circuit photovoltages (Voc) often exceed those of electrolyte-based DSSCs due to a smaller energy loss during the dye regeneration process. However, the overall photovoltaic conversion efficiency of SS-DSSCs attained, currently with standard ruthenium complexes [91-92], or organic dyes [88], remains significantly below those of electrolyte-based devices. The smaller J$_{sc}$ values arise from the fact that the SS-DSSC employs only 1.5 to 3 μm-thick nanocrystalline TiO$_2$ films to ascertain quantitative collection of the photogenerated charge carriers and complete pore filling by the hole conductor. As the solar light harvesting by such thin films depends strongly on the optimized cross-section of the sensitizer, the use of a high-molar extinction-coefficient dye in combination with thin mesoporous TiO$_2$ electrodes is advantageous.

Recent advances in the photovoltaic performance of the SS-DSSC have augmented the power conversion efficiencies from the initial 0.74% [94], to in the range of about 5-7% [95-98]. Recently this maximum value was reported to be 15% for the SS-DSSC.
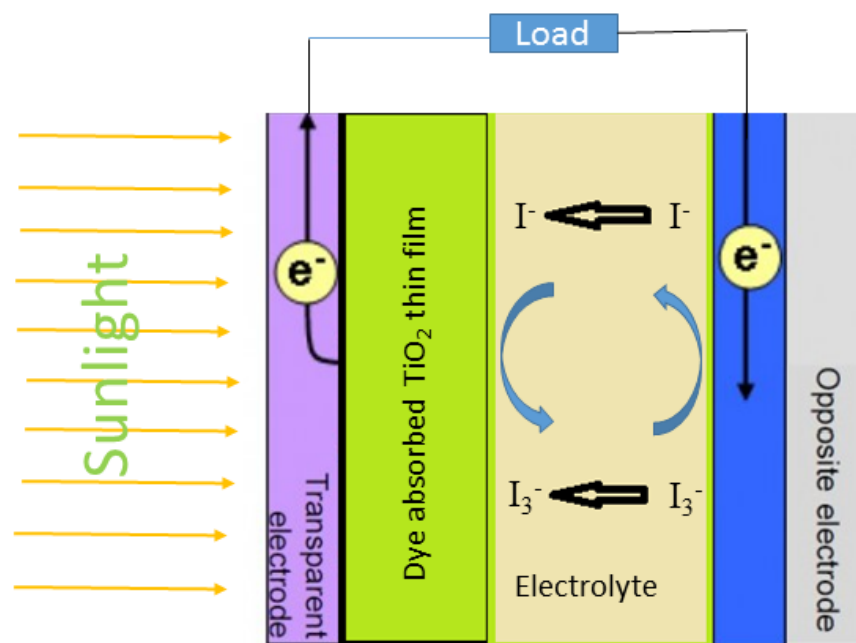
Figure 9. Schematic of TiO2 based dye sensitized solar cell.

Liu et al. [99] recently reported 3.2% conversion efficiency for the SS-DSSC by using poly (3-hexylthiophene) (P3HT) as organic dye sensitizer (hole transport material). They used spin coating and doctor blade techniques to prepare 2 μm thick layer of TiO_2 as a dense layer to control short circuiting and nanoscale thin film as electrode. The calcination was carried out at 500°C and a cell was obtained with enhanced properties of Voc, Jsc, FF and efficiency values of 880 mV, 8.22 mA/cm^2, 0.44, and 3.21%, respectively. Xue et al. [100-101] recently studied the properties of TiO_2 SS-DSSCs fabricated on flexible Ti foil. Platinum was used as the cathode and poly (3-hexylthiophene) as electrolyte which significantly increases the absorption of the light incident from back side. The reflective and absorptive properties of platinum and electrolyte were utilized to attain an SS-DSSC with 1.27% efficiency, 0.94 V open circuit voltage (V_{oc}), 2.85 mAcm^{-2} short circuit current density (J_{sc}), and 0.47 fill factor (FF). The lower efficiency was attributed to the reflective properties (80% transmittance) of platinum coupled with the electrolyte. Umar et al. [102] reported the synthesis of proliferous TiO_2 micro-tablets (PTM) with surface decorated by nanowires grown on the ITO surface. It was observed that the performance of the nanostructured (nanowires on surface and nano-cuboids in the interior) device depended on the density of the PTM, and the best results were achieved with a high

density of PTM and low inter-PTM overlapping. However, the efficiency is quite low compared to those reported TiO_2 based DSSCs. The limitation of electron transport, the chemical stability of the electrolyte and dye are the main issues related to low efficiency.

The efficiency of the DSSCs can be enhanced by preventing the back electron flow using a blocking layer of TiO_2 between FTO and electrolyte [103]. Sangiorgi et al. [104] reported the importance of this blocking layer in DSSC by comparing the electrical properties of the device with and without a blocking layer.

In addition to TiO_2, ZnO, Au, graphene oxide and Nb_2O_5 layers were also reported as blocking layers by a number of groups. Liu et al. [105] reported the effect of all blocking layers on the properties of DSSC and reported that ZnO is advantageous over TiO_2 and other layers. The thickness of the blocking layer must not exceed 300 nm in order to prevent the blocking layer from charge trap [105].

The introduction of foreign dopant in TiO_2 was also reported for enhancing the properties of the DSSC device [106]. The effect of doping Zn on TiO_2 was studied by Niaki et al. [107] and stated that Zn^{2+} has lower numbers of valance electrons than those of TiO_2^{4+}, therefore, excess of holes are created by generating an accepter band near TiO_2 valance band which helps in migration of electrons between bands.

Kuang et al. [108] reported that the length of TiO_2 nanotubes influences the properties of the DSSCs, and they studied 5-14 μm long nanotube arrays whose length was controlled by the anodization duration. The nanotubes reduce the adsorption of dyes on TiO_2 surface due to decrease in the surface area which reduces the properties of the DSSCs. Yang et al. [109] reported the treatment of $TiCl_4$ on TiO_2 nanotubes (TNT) to overcome this problem. The study was also carried out for a composite film of TNT (10 wt%) and TiO_2 nanoparticles dipped for 30 minutes in 60 mM solution of $TiCl_4$ at 70°C for 30 minutes and annealed at 450°C for 15 min.

Mathew et al. [110] recently reported the DSSCs with an efficiency of 13% by engineering the structure of TiO_2. In nanostructured materials, the nanoparticles of TiO_2 are predominant in

achieving a maximum efficiency attributing to the large surface area of nano particles. Further decreasing the size of the particle is expected to decrease the pore size and increase the defect sites as well as the grain boundaries, which will lower the solar cell performance. An optimum size of the particle must be identified along with the suitable dyes that will be helpful in attaining the maximum efficiency for the DSSCs [111].

3.2   ZnO nanowires

Nano structured zinc oxide is recently used as a multi-function material in solar cells. ZnO has a wide band gap with higher electron mobility than TiO_2 which can overcome a high electron recombination. However, the efficiency of nanostructured ZnO material is lower than that of the TiO_2, and few studies on ZnO nanostructured DSSC solar cells have achieved a high conversion efficiency [112]. Martinson reported that the surface morphologies of ZnO are more amenable in comparison to TiO_2 which increases the dye loading capacity and decreasing the recombination effect inside the DSSC. Many ZnO nanostructures have been fabricated, including nanowires, nanoparticles, nanocombs, nanoflowers, nanobelts, nanoflakes, nanoclusters, nanotubes, porous nano-sheets, nano-colloids, and nano-powders [113-118]. The results of the DSSCs were made by the ZnO nanotubes, nanowires and other 1D to 2D nanostructured photoanodes indicated that the special morphology can provide a unique advantage for electron transport. Instead of random/zigzag pathway in the particle-based photoanode, they provide unidirectional conduction paths for electrons inside the photo anode [118]. Cheng et al. [118] reported the synthesis of ZnO nanowires using a modified aqueous solution method for the DSSC on seeded fluorine-doped tin oxide (FTO) substrates. The nano wires were coated with the ZnO nanoparticles by dip coating techniques followed by the growth of branched ZnO nanowires. The DSSCs using standard nanowire was also studied in comparison with the branched ZnO nanowires DSCC.

Choi et al. [119] reported yttrium doped zinc oxide (ZnO) nanowires for DSSC on seedless ITO substrates. It was observed that the yttrium ions inhibited the nucleation of ZnO which caused a decrease in the density of ZnO nanowires. When the concentration of the yttrium ions was increased, the increase in the diameter of the ZnO nanowires was observed. [113]. Hsu and Chang [120] reported that Ag doped ZnO nanorods grown on stainless steel (SS) mesh were an efficient visible-light photo-catalysts with high activity and stability. Ag doped ZnO nano rods

not only increased the surface area of photocatalysts but also enhanced red-shift in the absorption band and improved the visible light absorption capacity [120]. Chae et al. [121] reported ZnO nanorods grown hydrothermally with fast growth rate and high packing density on SS wire for making the DSSC. They observed the long durability of the device attributed to the strong adhesive properties between ZnO and SS wire. It was reported that a longer dye loading time degraded ZnO nano rods which ultimately affected the solar cell parameters. The ideal dye loading time was optimized to be two hours [122] which leads to an efficiency of 2.57 %.

Gondoni et al. [123] reported the Al doped ZnO nano and meso-architectures for enhancing light harvesting properties using a pulsed laser ablation method. The use of Al doped ZnO as the TCO for ZnO nanostructured DSSCs can reduce the lattice mismatching and improve adhesion for obtaining a durable and sustainable DSSC. ZnO was also applied as a hole blocking layer in DSSC [122]. A thin compact ZnO layer (<200 nm) with high electron mobility and high transmittance (100%) of visible light has increased the efficiency and degradation time. The performance of such a cell was maintained reliably even after 200 days. Chou et al. reported [124] ZnO nanowires with an average length of 6 μm and diameter of 100 nm and ZnO nano particles of average size of 50-60 nm . Thin films of ZnO nanowires immersed in an inert solution of ethanol containing ZnO nanoparticles could serve as a semiconductor layer and CdS (or CdS/CdSe) as sensitizing layer for fabrication of the DSSCs. The efficiency of composite layer ZnO/CdS showed an efficiency of 0.24%, which is twice as high as that of the bare ZNW/CdS (0.12%) and ~33% higher than with bare ZNP/CdS (0.18%).

Law et al. [125] reported core-shell ZnO nanowires DSSC with alumina shell as insulating blocking layer to improve the short circuit voltage. The blocking layer can efficiently tunnel electrons and thus can enhance efficiency to 2.25%. This enhanced efficiency could be due to the single crystalline nature and radial surface electric field for each nanowire. An efficiency of 4.8% has been reported by Xu et al. [126] using hierarchical structure nanowires and nano-sheet photo-anode. The maximum efficiency for ZnO nanostructured (5.41%) reported by C.-Y. Lin et al. [127] using the ZnO nanosheet synthesized by chemical bath deposition technique. Similarly some researchers modify the ZnO nanostructures for improving injection efficiency and reducing the recombination effect caused by Zn^{2+}/dye complex. Core-shell structured TiO_2-ZnO

nanostructures have been considered as promising candidates to solve this problem. With TiO_2 shell, the electron injection efficiency can be maintained at normal level for most of commonly used dye. Additional, by applying TiO_2 shell on ZnO can not only improve the structure stability but also form an n-n+ heterojunction which can prevent the injected electrons from accumulating at the top surface of the ZnO nanostructures [128-129].

Chao et al. [130] recently used two sequential low-temperature processes to achieve a core-shell structure. To reduce and/or the process temperature, combination of hydrothermal growth of ZnO and plasma ion assisted evaporation of crystalline TiO2 shell were employed. By adjusting deposition parameters, ZnO nanorods can be homogeneously covered with a layer of anatase TiO_2 nanostructure to form core-shell nanorods and nano-sculptured foxtail-like patterns (In Fig. 11 (a) and (b)). Power conversion efficiency of DSSCs were improved from 0.3% to 1.8% after using the ZnO/TiO_2 hybrid structure due to reduced recombination as well as dye loading. By using these low temperature techniques with a self-designed *in-situ* microfluidic control unit assistant hydrothermal process, flexible DSSCs based on turntable ZnO/TiO_2 to Al doped ZnO/TiO_2 nanostructures (see Fig. 10 (c) and (d)) with highest average PCE of 4.5% was achieved. [131] The Al doped ZnO nanostructure core improved the accessible surfaces (i.e. benefit from improving dye loading) with a demand for a long range electronic connectivity (i.e. reducing recombination), thus improve the power conversion efficiency.
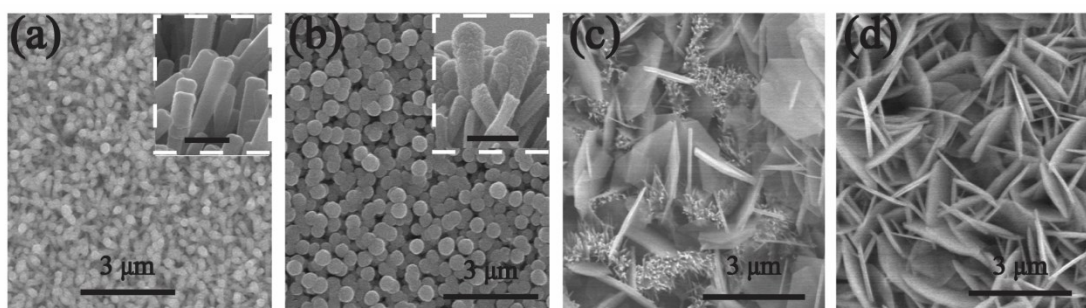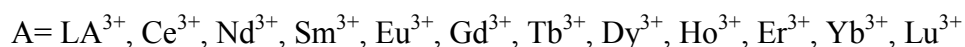

Fig 10, Represented SEM images of the as synthesized ZnO/TiO2 hybrid (a) nanorods (b) foxtail-liked nanostructure; and (c) hybrid nanostructure composite Al doped ZnO nanoflakes with ZnO nanorods (d) Al doped ZnO nanoflakes.
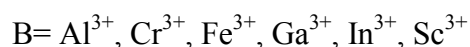
4. Perovskite solar cell

4.1 Recent progress in efficient hybrid lead halide perovskite solar cells

The DSSCs are promising low cost solar cells with merits of simple and clean fabrication, low cost and abundant raw material, and offer the possibilities to design solar cells with a large flexibility in shape, color, and transparency. Integration into different products opens up new commercial opportunities [103,132]. However, concern over leakage of the liquid electrolyte has caused a bottleneck in rapid development and commercialisation, therefore, there need new designs of solid-state sensitized solar cells to replace the liquid electrolyte with hole-transporting material (HTM). Currently molecular HTM of 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiroMeOTAD) are the most popular in solid-state DSSCs. However, the photovoltaic performance of solid-state DSSCs containing polymeric HTMs was generally inferior to those containing molecular spiro-MeOTAD because of the difficult infiltration of the long-chain polymers into the mesopores. In order to absorb most of the incident sunlight, the porous TiO_2 film is required to be as thick as 10 μm to provide sufficient internal surface area to adsorb sufficient dyes. That is impractical for the SS-DSSCs. Alternatively, the sensitizers with a high extinction coefficient or wide absorption spectrum such as quantum dots enable more sufficient sunlight absorption in much thin films. In 2012, a breakthrough in the DSSCs was achieved using organometallic halides $CH_3NH_3PbI_3$ having a perovskite structure. The reported photo-to-electron conversion efficiency (PCE) for mesoporous TiO_2 film adsorbed with perovskite $CH_3NH_3PbI_3$ nanocrystals was 9.7% under AM1.5 illumination in 2012 [133]. Such a revolution encouraged the scientists and researchers to focus their attention on perovskite structured material. Currently, the perovskite material has become a new development in the field of photovoltaic with over 20.1% conversion efficiency [134].

The general stoichiometry of the perovskite structure consists of ABX_3, where "A" and "B" are cations and X is anion. A and B consist of the following elements such that A being larger than B [135-136].

$A= LA^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+}, Lu^{3+}$

B= Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}

Perovskite is an organometallic halide used as a sensitizer as well as a hole and electron conductor. By combining these two approaches in a solar cell, the efficiency of perovskite material increases abruptly. $CsSnI_3$ perovskite as solid state DSSC with 8.5% efficiency was reported by Chung et al. [136] soon after the discovery of the perovskite in photovoltaics. In the same year, another group reported efficiency of 8.0% using perovskite methylamonium lead iodide chloride ($CH_3NH_3PbI_2Cl$) as light absorber and TiO_2 as a transparent n-type counterpart. The same group reported 11% efficiency by replacing the photo-electrode (TiO_2) by an insulating Al_2O_3 in combination with perovskite material [137]. The use of thin film configuration of the perovskite solar cell was introduced to deposit the film directly on TiO_2 compact layer in order to avoid any mesoporous layer. Liu et al. [138] used vapour deposited perovskite film onto TiO_2 films and reported an efficiency of 15.4%. Kumar et al. [139] employed two different approaches for the deposition of ZnO as a blocking layer on FTO and ITO coated substrates. The $CH_3NH_3PbI_3$ was spin-coated on electrodeposited ZnO on FTO and ITO substrates in the 1st approach. In the 2nd approach, 5 nm ZnO nanoparticle thin films was utilized in the assembly of planner solar cell based on ITO and FTO substrate. 15.7% and 10.2% efficiencies were recorded for the perovskite devices on the FTO and ITO substrates respectively [138, 140]. Burschka et al. [141] reported 15% efficiency for perovskite sensitized hybrid solar cell employing two different techniques, spin coating and sequential deposition on mesoporous TiO_2. It is noted that the high efficiency is however precluded with the sensitive nature of organic absorber. For planar heterojunction perovskite solar cell conversion efficiency of 15.4% was also reported [133, 142]. Seok's group in 2013 reported 16.2% efficiency for perovskite solar cell by using $CH_3NH_3PbI_{3-x}Br_x$ (10–15% Br) and a poly-triarylamine hole transporting medium. Two additional discrete layers of perovskite materials were used in the solar cell structure instead of one continuous perovskite layer to provide scaffolding. This scaffolding is the key in enhancing the efficiency of the solar cell [142].

Perovskite materials were initially utilized as sensitizer in DSSC because of the ionic nature of perovskite. The liquid hole transmitting medium (HTM) was recently replaced by solid HTM for long term stability of the solar cell by a Korean group, and they reported an efficiency of 17.9%

[145]. Recently, slightly over 20% efficiency was claimed to be achieved with a solid state $CH_3NH_3PbX_3$ based solar cell device [146]. The organometallic halide perovskite absorbers have better properties than metal chalcogenide quantum dots, though they have the same absorption coefficient [120, 136].

4.2   Hysteresis and stability

Perovskite solar cells have achieved a great success with efficiencies now exceeding 20%. However, a certain class of perovskite solar cell, particularly organometal trihalide perovskites, exhibits photocurrent hysteresis. Therefore, it is essential that the origins and mechanisms of the I–V hysteresis are fully understood to minimize or eradicate these hysteresis effects for practical applications. This hysteresis has been tentatively attributed to the para-electric or ferroelectric properties of perovskites at room temperature and above [147-148]. Simulations suggest that the internal electrical fields associated with microscopic polarization domains contribute to hysteretic anomalies in the current-voltage response of PSCs due to variations in electron-hole recombination in the bulk [147]. However, others would suggest that, because of its low lattice energy, organometal halide perovskite tends to possess a strong ionic characteristics, which is sensitive to polarization in an electric field [148]. Impedance study shows that a high value of the dielectric constant at low frequencies results from a combination of dipolar, ionic and electronic contributions is the main reason for the J/V hysteresis [149].

In general, $CH_3NH_3PbI_3$ crystals are prepared using solution process via one-step or two-step, depending on whether the precursor solution (PbI_2 and CH_3NH_3I) are deposited onto the substrate once or sequentially. In using a one-step processing technique it is difficult to achieve optimal single crystal perovskite thin films due to multiple $CH_3NH_3PbI_3$ seed clusters [150], whereas with the sequential deposition method it is hard to ensure purity of the resultant $CH_3NH_3PbI_3$ as the residual organic component introduces a poor stability [151]. Finally, good crystallite characteristics of $CH_3NH_3PbI_3$ is crucially important to benefit device performance and material stability since defects within perovskite crystallites and at the interfaces can trap photogenerated charges or accelerate the mobile species migrating through $CH_3NH_3PbI_3$ [152].

The stability of CH₃NH₃PbI₃ films also depend significantly on a variety of environmental factors including temperature, radiation, oxygen and moisture [153]. In this case, a proper encapsulation or layer-by-layer approach should be applied to improve device stability by avoiding any contact with these egregious factors. However, it is not sufficient to guarantee their long-term stability since the CH₃NH₃PbI₃ has an intrinsic nature of thermal instability [154]. Thermo-gravimetric analysis and chemical analysis results indicated that CH₃NH₃PbI₃ suffers from an irreversible photo-degradation and a subsequent loss of organic cation component even in absence of oxygen and moisture with temperature higher 85° [154].

To date, Spiro-OMeTAD is widely used as the hole selective material in solid-state perovskite devices. However, the pristine spiro-OMeTAD suffers from low carrier mobility due to amorphous nature. Thus, Li ions are used as additives to increase conductivity of spiro-OMeTAD as well as allow a stable doping level in the oxygen atmosphere, and cobalt complexes have also been used as p-type dopants. However, such additives still bring several disadvantages, including long-term stability in spiro-OMeTAD and moisture-induced degradation in CH₃NH₃PbI₃ [155]. As a result, tremendous efforts have been focused on replacing spiro-OMeTAD. Besides organic molecule HTMs, inorganic materials such as CuSCN [156], CuI [157], and NiO [158] have also been employed to serve as low cost hole extraction materials with long-term stability indicating practical potential. Among them, NiO has been one successful candidate due to its ideal energy level, high carrier mobility and various approaches for synthesis and processing including sol-gel, sputtering and doctoral blading.

5. Conclusions and Future

The present review focuses on the recent development of highly efficient solar cells using nanoscale materials and tailoring desired nanostructures using new materials, new structures and band-gap engineering. The efficient solar cell material for commercialization requires more resources apart from the current materials available in the market. Currently, CZTS and CdTe are commericallised thin film based solar cells.

- The selenization of the CZTS film is promsing to increase the efficiency of solar cells and can be carried out by annealing the sulfurized (CZTS) film in selenium containing atmosphere. It is also possible to increase the efficiency of CZTS-based solar cell to include uniform and adherent back contact and side-stepping of the carbon which will decrease the crystallinity and optical transmission in the solar cell. The improvement in the cell efficiency can be boosted in three potential ways. One way is to develop a new powerful photosensitizer with broad spectral range and higher molar extinction coefficient than the existing sensitizers. Secondly, the improvement in open circuit voltage which is the difference between quasi fermi level in semiconductor and redox couple in electrolyte. The use of suitable electrolyte can boost the value of open circuit voltage for a particular semiconductor. The loss of energy must be controlled in solar cell operation and this is also a viable option to increase the efficiency of the solar cell. It is possible to reduce energy losses from charge recombination, electron trapping, optical reflections etc.

- For the DSSCs, the nanostructured metal oxides have ability to attain high efficiency as they have several scales of pores which can adsorb dye for nonporous scaffold configuration. The dyesensitized solar cell efficiency is 10-11% for many years, and this value is very far from the theoretically speculated value, while the reported efficiency for perovskite cell is 20.1%, thus perovskite based solar cells become dominant.

- The rapid rate of progress in p-type DSSC combined with the existence of clear avenues for device optimization, suggested the promising future of p-type DSSC. The p-type DSSC is a new and exciting photovoltaic field for research.

- The nanostructured solar cell is also a revolutionary change in the field of photovoltaics. In perovskite materials, $CH_3NH_3PbI_3$, Pb is a toxic element. Replacing Pb by Sn or Sb can reduce the toxicity in the perovskite materials. The result must be verified by Ab-initio calculations for the identification of new families.

- Perovskite is one of the most promising candidates for the future photovoltaics technology with advantages of low processing costs and simple execution for attractive products, such as flexible and transparent. Perovskite tandem cell modules are promising for commercialization along with direct integration with other cell technologies with Si and SIGS for high-performance tandem cells..

Acknowledgement

References

[1] Economic UN, Asia SCf, Pacific t. Guidebook on Promotion of Sustainable Energy Consumption: Consumer Organizations and Efficient Energy Use in the Residential Sector: UN; 2002.

[2] Asim N, Sopian K, Ahmadi S, Saeedfar K, Alghoul MA, Saadatian O, et al. A review on the role of materials science in solar cells. Renewable and Sustainable Energy Reviews. 2012;16:5834-47.

[3] Dhakal TP, Peng CY, Reid Tobias R, Dasharathy R, Westgate CR. Characterization of a CZTS thin film solar cell grown by sputtering method. Solar Energy. 2014;100:23-30.

[4] Thimsen EJ, Washington University in St. Louis. Energy E, Engineering C. Metal Oxide Semiconductors for Solar Energy Harvesting: Washington University in St. Louis; 2009.

[5] Twidell J, Weir T. Renewable energy resources: Routledge; 2015.

[6] Goldschmidt JC, Fischer S. Upconversion for Photovoltaics–a Review of Materials, Devices and Concepts for Performance Enhancement. Advanced Optical Materials. 2015;3:510-35.

[7] Aberle AG. Thin-film solar cells. Thin Solid Films. 2009;517:4706-10.

[8] Green, M. A., et al. (2015). "Solar cell efficiency tables (Version 45)." Progress in Photovoltaics: Research and Applications 23(1): 1-9.

[9] Rahman MZ. Advances in surface passivation and emitter optimization techniques of c-Si solar cells. Renewable and Sustainable Energy Reviews. 2014;30:734-42.

[10] Pandey, A. K., et al. (2016). "Recent advances in solar photovoltaic systems for emerging trends and advanced applications." Renewable and Sustainable Energy Reviews 53: 859-884.

[11] Cui H, Campbell PR, Green MA. Optimisation of the Back Surface Reflector for Textured Polycrystalline Si Thin Film Solar Cells. Energy Procedia. 2013;33:118-28.

[12] Kang D-W, Kwon J-Y, Shim J, Lee H-M, Han M-K. Highly conductive GaN anti-reflection layer at transparent conducting oxide/Si interface for silicon thin film solar cells. Solar Energy Materials and Solar Cells. 2012;105:317-21.

[13] Jang J, Kim M, Kim Y, Kim K, Baik SJ, Lee H, et al. Three dimensional a-Si:H thin-film solar cells with silver nano-rod back electrodes. Current Applied Physics. 2014;14:637-40.

[14] Heo YH, You DJ, Lee H, Lee S, Lee H-M. ZnO:B back reflector with high haze and low absorption enhanced triple-junction thin film Si solar modules. Solar Energy Materials and Solar Cells. 2014;122:107-11.

[15] Kim S, Chung J-W, Lee H, Park J, Heo Y, Lee H-M. Remarkable progress in thin-film silicon solar cells using high-efficiency triple-junction technology. Solar Energy Materials and Solar Cells. 2013;119:26-35.

[16] Wu D, He J, Zhang S, Cao K, Gao Z, Xu F, et al. Multi-dimensional titanium dioxide with desirable structural qualities for enhanced performance in quantum-dot sensitized solar cells. Journal of Power Sources. 2015;282:202-10.

[17] Sriprapha K, Hongsingthong A, Krajangsang T, Inthisang S, Jaroensathainchok S, Limmanee A, et al. Development of thin film a-SiO:H/a-Si:H double-junction solar cells and their temperature dependence. Thin Solid Films. 2013;546:398-403.

[18] Li Y, Chen Q, He D, Li J. Radial junction Si micro/nano-wire array photovoltaics: Recent progress from theoretical investigation to experimental realization. Nano Energy. 2014;7:10-24.

[19] Du C-H, Wang T-Y, Chen C-H, Yeh JA. Fabrication of an ultra-thin silicon solar cell and nano-scale honeycomb structure by thermal-stress-induced pattern transfer method. Thin Solid Films. 2014;557:372-5.

 [20] Luque A, Hegedus S. Handbook of Photovoltaic Science and Engineering: Wiley; 2011.

[21] R. Catchpole K, J. McCann M, J. Weber K, W. Blakers A. A review of thin-film crystalline silicon for solar cell applications. Part 2: Foreign substrates. Solar Energy Materials and Solar Cells. 2001;68:173-215.

[22] Guo, Q., et al. (2010). "Fabrication of 7.2% efficient CZTSSe solar cells using CZTS nanocrystals." Journal of the American Chemical Society **132**(49): 17384-17386.

[23] Mathew, S., et al. (2014). "Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers." Nature chemistry **6**(3): 242-247.

[24] Noh, J. H., et al. (2013). "Chemical management for colorful, efficient, and stable inorganic–organic hybrid nanostructured solar cells." Nano Letters **13**(4): 1764-1769.

[25] Shin, B., et al. (2013). "Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant Cu2ZnSnS4 absorber." Progress in Photovoltaics: Research and Applications **21**(1): 72-76.

[26] Wang, W., et al. (2014). "Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency." Advanced Energy Materials **4**(7).

[27] M. Gloeckler, I. Sankin, Z. Zhao (2013). "CdTe Solar Cells at the Threshold to 20%"(PDF). *IEEE Journal of Photovoltaics* **3** (4): 1389–1393.

[28] Green, M. A., et al. (2015). "Solar cell efficiency tables (Version 45)." Progress in Photovoltaics: Research and Applications **23**(1): 1-9.

[29] Europ. Opt. Soc. Rap. Public. **9,** 14052 (2014) www.jeos.org

[32] Park S, Cho E, Song D, Conibeer G, Green MA. n-Type silicon quantum dots and p-type crystalline silicon heteroface solar cells. Solar Energy Materials and Solar Cells. 2009;93:684-90.

[33] Hsu C-H, Wu J-R, Lu Y-T, Flood DJ, Barron AR, Chen L-C. Fabrication and characteristics of black silicon for solar cell applications: An overview. Materials Science in Semiconductor Processing. 2014;25:2-17.

[34] Kegel J, Angermann H, Stürzebecher U, Conrad E, Mews M, Korte L, et al. Over 20% conversion efficiency on silicon heterojunction solar cells by IPA-free substrate texturization. Applied Surface Science. 2014;301:56-62.

[35] Becker C, Amkreutz D, Sontheimer T, Preidel V, Lockau D, Haschke J, et al. Polycrystalline silicon thin-film solar cells: Status and perspectives. Solar Energy Materials and Solar Cells. 2013;119:112-23.

[38] Birkmire RW, Eser E. POLYCRYSTALLINE THIN FILM SOLAR CELLS:Present Status and Future Potential. Annual Review of Materials Science. 1997;27:625-53.

[39] Spalatu N, Hiie J, Valdna V, Caraman M, Maticiuc N, Mikli V, et al. Properties of the CdCl2 Air-annealed CSS CdTe Thin Films. Energy Procedia. 2014;44:85-95.

[40] Ferekides CS, Balasubramanian U, Mamazza R, Viswanathan V, Zhao H, Morel DL. CdTe thin film solar cells: device and technology issues. Solar Energy. 2004;77:823-30.

[41] Gloeckler M, Sankin I, Zhao Z. CdTe Solar Cells at the Threshold to 20% Efficiency. Photovoltaics, IEEE Journal of. 2013;3:1389-93.

[42] Kranz L. Doping of polycrystalline CdTe for high-efficiency solar cells on flexible metal foil. Nature Commun. 2013;4:2306.

[43] Johs B, Hale JS. Dielectric function representation by B-splines. physica status solidi (a). 2008;205:715-9.

[44] Johs B, Hale JS. Dielectric function representation by B-splines. physica status solidi (a). 2008;205:715-9.

[45] Gong J, Liang J, Sumathy K. Review on dye-sensitized solar cells (DSSCs): fundamental concepts and novel materials. Renewable and Sustainable Energy Reviews. 2012;16:5848-60.

[46] Krebs FC. Fabrication and processing of polymer solar cells: a review of printing and coating techniques. Solar Energy Materials and Solar Cells. 2009;93:394-412.

[47] Li B, Wang L, Kang B, Wang P, Qiu Y. Review of recent progress in solid-state dye-sensitized solar cells. Solar Energy Materials and Solar Cells. 2006;90:549-73.

[48] Green, M. A., et al. (2015). "Solar cell efficiency tables (Version 45)." Progress in Photovoltaics: Research and Applications **23**(1): 1-9.

[49] Nichterwitz M, Caballero R, Kaufmann CA, Schock H-W, Unold T. Generation-dependent charge carrier transport in Cu(In,Ga)Se2/CdS/ZnO thin-film solar-cells. Journal of Applied Physics. 2013;113:-.

[50] Saleh BEA, Teich MC. Fundamentals of Photonics: Wiley; 2013.

[51] Kim H, Cha K, Fthenakis VM, Sinha P, Hur T. Life cycle assessment of cadmium telluride photovoltaic (CdTe PV) systems. Solar Energy. 2014;103:78-88.

[52] Bhosale SM, Suryawanshi MP, Gaikwad MA, Bhosale PN, Kim JH, Moholkar AV. Influence of growth temperatures on the properties of photoactive CZTS thin films using a spray pyrolysis technique. Materials Letters. 2014;129:153-5.

[53] Life Cycle Inventories and Life Cycle Assessments of Photovoltaic Systems IEA PVPS Task 12, Subtask 2.0, LCA Report IEA-PVPS 12-04:2015 ISBN 978-3-906042-28-2

[54] Shockley W, Queisser HJ. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. Journal of Applied Physics. 1961;32:510-9.

[55] Yu WW, Qu L, Guo W, Peng X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. Chemistry of Materials. 2003;15:2854-60.

[56] Jun HK, Careem MA, Arof AK. Quantum dot-sensitized solar cells—perspective and recent developments: A review of Cd chalcogenide quantum dots as sensitizers. Renewable and Sustainable Energy Reviews. 2013;22:148-67.

[57] Gessert TA, Wei SH, Ma J, Albin DS, Dhere RG, Duenow JN, et al. Research strategies toward improving thin-film CdTe photovoltaic devices beyond 20% conversion efficiency. Solar Energy Materials and Solar Cells. 2013;119:149-55.

[58] Wang, X. and Z. M. Wang (2013). High-Efficiency Solar Cells: Physics, Materials, and Devices, Springer International Publishing.

[59] Hanna MC, Nozik AJ. Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. Journal of Applied Physics. 2006;100:-.

[60] Semonin OE, Luther JM, Choi S, Chen H-Y, Gao J, Nozik AJ, et al. Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. Science. 2011;334:1530-3.

[61] Smith PPK, Parise JB. Structure determination of SnSb2S4 and SnSb2Se4 by high-resolution electron microscopy. Acta Crystallographica Section B. 1985;41:84-7.

[62] Beard MC, Knutsen KP, Yu P, Luther JM, Song Q, Metzger WK, et al. Multiple Exciton Generation in Colloidal Silicon Nanocrystals. Nano Letters. 2007;7:2506-12.

[63] Song Y, Feng D, Shi W, Li X, Ma H. Parallel comparative studies on the toxic effects of unmodified CdTe quantum dots, gold nanoparticles, and carbon nanodots on live cells as well as green gram sprouts. Talanta. 2013;116:237-44.

[64] Xiao J, Bai Y, Wang Y, Chen J, Wei X. Systematic investigation of the influence of CdTe QDs size on the toxic interaction with human serum albumin by fluorescence quenching method. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2010;76:93-7.

[65] Dale PJ, Peter LM, Loken A, Scragg J. Towards Sustainable Photovoltaic Solar Energy Conversion: Studies Of New Absorber Materials. ECS Transactions. 2009;19:179-87.

[66] Chen S, Gong XG, Walsh A, Wei S-H. Crystal and electronic band structure of Cu2ZnSnX4 (X=S and Se) photovoltaic absorbers: First-principles insights. Applied Physics Letters. 2009;94:-.

[67] Nitsche R, Sargent DF, Wild P. Crystal growth of quaternary 122464 chalcogenides by iodine vapor transport. Journal of Crystal Growth. 1967;1:52-3.

[68] Ali N, Ahmed R, ul Haq B, Shaari A, Hussain R, Goumri-Said S. A novel approach for the synthesis of tin antimony sulphide thin films for photovoltaic application. Solar Energy. 2015;113:25-33.

[69] Pawar SM, Moholkar AV, Kim IK, Shin SW, Moon JH, Rhee JI, et al. Effect of laser incident energy on the structural, morphological and optical properties of Cu2ZnSnS4 (CZTS) thin films. Current Applied Physics. 2010;10:565-9.

[70] Seol J-S, Lee S-Y, Lee J-C, Nam H-D, Kim K-H. Electrical and optical properties of Cu2ZnSnS4 thin films prepared by rf magnetron sputtering process. Solar Energy Materials and Solar Cells. 2003;75:155-62.

[71] Yoo H, Kim J. Comparative study of Cu2ZnSnS4 film growth. Solar Energy Materials and Solar Cells. 2011;95:239-44.

[72] Wang H. Progress in thin film solar cells based on Cu 2 ZnSnS 4. International Journal of Photoenergy. 2011;2011.

[73] Kodigala SR. Thin Film Solar Cells From Earth Abundant Materials: Growth and Characterization of Cu2(ZnSn)(SSe)4 Thin Films and Their Solar Cells: Elsevier Science; 2013.

[74] Abermann S. Non-vacuum processed next generation thin film photovoltaics: Towards marketable efficiency and production of CZTS based solar cells. Solar Energy. 2013;94:37-70.

[75] Zhang, S. (2010). <u>Organic Nanostructured Thin Film Devices and Coatings for Clean Energy</u>, CRC Press.

[76] Jassim, S. A.-J., et al. (2013). "Influence of substrate temperature on the structural, optical and electrical properties of CdS thin films deposited by thermal evaporation." <u>Results in Physics</u> **3**: 173-178.

[77] Jiang M, Yan X. Cu2ZnSnS4 Thin Film Solar Cells: Present Status and Future Prospects2013.
[78] Kosyachenko LA, Mathew X, Roshko VY, Grushko EV. Optical absorptivity and recombination losses: The limitations imposed by the thickness of absorber layer in CdS/CdTe solar cells. Solar Energy Materials and Solar Cells. 2013;114:179-85.
[79] Park S-W, Kim D-I, Lee T-S, Lee K, Yoon Y, Cho YH, et al. Solid-state selenization of printed Cu(In,Ga)S2 nanocrystal layer and its impact on solar cell performance. Solar Energy Materials and Solar Cells. 2014;125:66-71.
[80] Agilan S, Mangalaraj D, Narayandass SK, Mohan Rao G, Velumani S. Structure and temperature dependence of conduction mechanisms in hot wall deposited CuInSe2 thin films and effect of back contact layer in CuInSe2 based solar cells. Vacuum. 2010;84:1220-5.
[81] El-Naggar AM. Influence of thickness on the optical properties of vacuum-deposited a-Si:H films. Optics & Laser Technology. 2001;33:237-42.
[82] Gassoumi A, Kanzari M. Optical, structural and electrical properties of the new absorber Sn2Sb2S5 THIN FILMS. Chalcogenide Letters. 2009;6:163-70.
[83] Abdelkader D, Ben Rabeh M, Khemiri N, Kanzari M. Investigation on optical properties of SnxSbySz sulfosalts thin films. Materials Science in Semiconductor Processing. 2014;21:14-9.
[84] Fadhli Y, Rabhi A, Kanzari M. Effect of air annealing on dispersive optical constants and electrical properties of SnSb2S4 thin films. Materials Science in Semiconductor Processing. 2014;26:282-7.
[85] Ali N, Hussain ST, Khan Y, Ahmad N, Iqbal MA, Abbas SM. Effect of air annealing on the band gap and optical properties of SnSb2S4 thin films for solar cell application. Materials Letters. 2013;100:148-51.
[86] Ali, N., et al. (2015). "A novel approach for the synthesis of tin antimony sulphide thin films for photovoltaic application." <u>Solar Energy</u> **113**: 25-33.

[87] Wang Y, Hu J, Wu Y, Xu J, Lu J, Zhao H, et al. Radiation damage effects on double-junction GaInP2/GaAs solar cells. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 2014;330:76-81.
 [88] Mathew S, Yella A, Gao P, Humphry-Baker R, CurchodBasile FE, Ashari-Astani N, et al. Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. Nat Chem. 2014;6:242-7.
[89] Hara K, Arakawa H. Dye-Sensitized Solar Cells. Handbook of Photovoltaic Science and Engineering: John Wiley & Sons, Ltd; 2005. p. 663-700.
[90] Liu D, Liu F, Liu J. Effect of vanadium redox species on photoelectrochemical behavior of TiO2 and TiO2/WO3 photo-electrodes. Journal of Power Sources. 2012;213:78-82.
[91] Wang M, Grätzel C, Moon SJ, Humphry-Baker R, Rossier-Iten N, Zakeeruddin SM, et al. Surface Design in Solid-State Dye Sensitized Solar Cells: Effects of Zwitterionic Co-adsorbents on Photovoltaic Performance. Advanced Functional Materials. 2009;19:2163-72.
[92] Snaith HJ, Moule AJ, Klein C, Meerholz K, Friend RH, Grätzel M. Efficiency enhancements in solid-state hybrid solar cells via reduced charge recombination and increased light capture. Nano Letters. 2007;7:3372-6.
[93] Wang M, Xu M, Shi D, Li R, Gao F, Zhang G, et al. High-Performance Liquid and Solid Dye-Sensitized Solar Cells Based on a Novel Metal-Free Organic Sensitizer. Advanced Materials. 2008;20:4460-3.

[94] Bach U, Lupo D, Comte P, Moser J, Weissörtel F, Salbeck J, et al. Solid-state dye-sensitized mesoporous TiO2 solar cells with high photon-to-electron conversion efficiencies. Nature. 1998;395:583-5.

[95] Wang M, Liu J, Cevey-Ha N-L, Moon S-J, Liska P, Humphry-Baker R, et al. High efficiency solid-state sensitized heterojunction photovoltaic device. Nano Today. 2010;5:169-74.

[96] Wang M, Moon SJ, Zhou D, Le Formal F, Cevey-Ha NL, Humphry-Baker R, et al. Enhanced-Light-Harvesting Amphiphilic Ruthenium Dye for Efficient Solid-State Dye-Sensitized Solar Cells. Advanced Functional Materials. 2010;20:1821-6.

[97] Wang M, Moon SJ, Xu M, Chittibabu K, Wang P, Cevey-Ha NL, et al. Efficient and Stable Solid-State Dye-Sensitized Solar Cells Based on a High-Molar-Extinction-Coefficient Sensitizer. Small. 2010;6:319-24.

[98] Lu J, Chang YC, Cheng HY, Wu HP, Cheng Y, Wang M, et al. Molecular Engineering of Organic Dyes with a Hole-Extending Donor Tail for Efficient All-Solid-State Dye-Sensitized Solar Cells. ChemSusChem. 2015;8:2529-36.

[99] Liu Q, Li C, Jiang K, Song Y, Pei J. A high-efficiency solid-state dye-sensitized solar cell with P3HT polymer as a hole conductor and an assistant sensitizer. Particuology. 2014;15:71-6.

[100] Kalyanasundaram K. Dye-sensitized Solar Cells: EFPL Press; 2010.

[101] Xue Z, Wang L, Liu W, Liu B. Solid-state D102 dye sensitized/poly(3-hexylthiophene) hybrid solar cells on flexible Ti substrate. Renewable Energy. 2014;72:22-8.

[102] Ali Umar A, Nafisah S, Md Saad SK, Tee Tan S, Balouch A, Mat Salleh M, et al. Poriferous microtablet of anatase TiO2 growth on an ITO surface for high-efficiency dye-sensitized solar cells. Solar Energy Materials and Solar Cells. 2014;122:174-82.

[103] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-Sensitized Solar Cells. Chemical Reviews. 2010;110:6595-663.

[104] Sangiorgi A, Bendoni R, Sangiorgi N, Sanson A, Ballarin B. Optimized TiO2 blocking layer for dye-sensitized solar cells. Ceramics International. 2014;40:10727-35.

[105] Liu Y, Sun X, Tai Q, Hu H, Chen B, Huang N, et al. Influences on photovoltage performance by interfacial modification of FTO/mesoporous TiO2 using ZnO and TiO2 as the compact film. Journal of Alloys and Compounds. 2011;509:9264-70.

[106] Choudhury B, Choudhury A. Dopant induced changes in structural and optical properties of Cr3+ doped TiO2 nanoparticles. Materials Chemistry and Physics. 2012;132:1112-8.

[107] Ghanbari Niaki AH, Bakhshayesh AM, Mohammadi MR. Double-layer dye-sensitized solar cells based on Zn-doped TiO2 transparent and light scattering layers: Improving electron injection and light scattering effect. Solar Energy. 2014;103:210-22.

[108] Kuang D, Brillet J, Chen P, Takata M, Uchida S, Miura H, et al. Application of Highly Ordered TiO2 Nanotube Arrays in Flexible Dye-Sensitized Solar Cells. ACS Nano. 2008;2:1113-6.

[109] Yang J, Bark C, Kim K, Choi H. Characteristics of the Dye-Sensitized Solar Cells Using TiO2 Nanotubes Treated with TiCl4. Materials. 2014;7:3522-32.

[110] Mathews NR, Colín García C, Torres IZ. Effect of annealing on structural, optical and electrical properties of pulse electrodeposited tin sulfide films. Materials Science in Semiconductor Processing. 2013;16:29-37.

[111] Zhang Q, Cao G. Nanostructured photoelectrodes for dye-sensitized solar cells. Nano Today. 2011;6:91-109.

[112] Omar A, Abdullah H. Electron transport analysis in zinc oxide-based dye-sensitized solar cells: A review. Renewable and Sustainable Energy Reviews. 2014;31:149-57.

[113] Chu JB, Huang SM, Zhang DW, Bian ZQ, Li XD, Sun Z, et al. Nanostructured ZnO thin films by chemical bath deposition in basic aqueous ammonia solutions for photovoltaic applications. Applied Physics A. 2009;95:849-55.

[114] Liu Z, Li Y, Liu C, Ya J, Zhao W, E L, et al. Performance of ZnO dye-sensitized solar cells with various nanostructures as anodes. Solid State Sciences. 2011;13:1354-9.

[115] Shishiyanu S, Chow L, Lupan O, Shishiyanu T. Synthesis and characterization of functional nanostructured zinc oxide thin films. ECS Transactions. 9 ed2006. p. 65-71.

[116] Wahab R, Ansari SG, Kim YS, Seo HK, Kim GS, Khang G, et al. Low temperature solution synthesis and characterization of ZnO nano-flowers. Materials Research Bulletin. 2007;42:1640-8.

[117] Kakiuchi K, Hosono E, Kimura T, Imai H, Fujihara S. Fabrication of mesoporous ZnO nanosheets from precursor templates grown in aqueous solutions. Journal of Sol-Gel Science and Technology. 2006;39:63-72.

[118] Cheng H-M, Chiu W-H, Lee C-H, Tsai S-Y, Hsieh W-F. Formation of Branched ZnO Nanowires from Solvothermal Method and Dye-Sensitized Solar Cells Applications. The Journal of Physical Chemistry C. 2008;112:16359-64.

[119] Woo Choi H, Lee K-S, David Theodore N, Alford TL. Improved performance of ZnO nanostructured bulk heterojunction organic solar cells with nanowire-density modified by yttrium chloride introduction into solution. Solar Energy Materials and Solar Cells. 2013;117:273-8.

[120] Hsu M-H, Chang C-J. Ag-doped ZnO nanorods coated metal wire meshes as hierarchical photocatalysts with high visible-light driven photoactivity and photostability. Journal of Hazardous Materials. 2014;278:444-53.

[121] Chae Y, Park JT, Koh JK, Kim JH, Kim E. All-solid, flexible solar textiles based on dye-sensitized solar cells with ZnO nanorod arrays on stainless steel wires. Materials Science and Engineering: B. 2013;178:1117-23.

[122] Chou TP, Zhang Q, Cao G. Effects of Dye Loading Conditions on the Energy Conversion Efficiency of ZnO and TiO2 Dye-Sensitized Solar Cells. The Journal of Physical Chemistry C. 2007;111:18804-11.

[123] Gondoni P, Mazzolini P, Russo V, Petrozza A, Srivastava AK, Li Bassi A, et al. Enhancing light harvesting by hierarchical functionally graded transparent conducting Al-doped ZnO nano- and mesoarchitectures. Solar Energy Materials and Solar Cells. 2014;128:248-53.

[124] Chou C-Y, Li C-T, Lee C-P, Lin L-Y, Yeh M-H, Vittal R, et al. ZnO nanowire/nanoparticles composite films for the photoanodes of quantum dot-sensitized solar cells. Electrochimica Acta. 2013;88:35-43.

[125] Law M, Greene LE, Radenovic A, Kuykendall T, Liphardt J, Yang P. ZnO–Al2O3 and ZnO–TiO2 Core–Shell Nanowire Dye-Sensitized Solar Cells. The Journal of Physical Chemistry B. 2006;110:22652-63.

[126] Xu F, Dai M, Lu Y, Sun L. Hierarchical ZnO Nanowire–Nanosheet Architectures for High Power Conversion Efficiency in Dye-Sensitized Solar Cells. The Journal of Physical Chemistry C. 2010;114:2776-82.

[127] Lin C-Y, Lai Y-H, Chen H-W, Chen J-G, Kung C-W, Vittal R, et al. Highly efficient dye-sensitized solar cell with a ZnO nanosheet-based photoanode. Energy & Environmental Science. 2011;4:3448-55.

[128] Park N-G. Perovskite solar cells: an emerging photovoltaic technology. Materials Today.

[129] Wu H, Li L, Liang L-Z, Liang S, Zhu Y-Y, Zhu X-H. Recent progress on the structural characterizations of domain structures in ferroic and multiferroic perovskite oxides: A review. Journal of the European Ceramic Society. 2015;35:411-41.

[130] C. Zhao, D. Child, Y. Hu, N. Robertson, D. Gibson, S. C. Wang, Y. Q. Fu, Low temperature growth of hybrid ZnO/TiO2 nano-sculptured foxtail-structures for dye-sensitized solar cells . RSC Adv. 2014, 4, 61153

[131] C. Zhao, J. Zhang, Y. Hu, N. Robertson, P. A. Hu, D. Child, D. Gibson, Y. Q. Fu, In-situ microfluidic controlled, low temperature hydrothermal growth of nanoflakes for dye-sensitized solar cells, Sci. Rep. 2015, 5, 17750.

[132] Wang M, Grätzel C, Zakeeruddin SM, Grätzel M. Recent developments in redox electrolytes for dye-sensitized solar cells. Energy & Environmental Science. 2012;5:9394-405.

[133] Park N-G. Organometal Perovskite Light Absorbers Toward a 20% Efficiency Low-Cost Solid-State Mesoscopic Solar Cell. The Journal of Physical Chemistry Letters. 2013;4:2423-9.

[134] Noh JH, Im SH, Heo JH,Mandal TH, Seok SI.Chemical Management for Colorful, Efficient, and Stable Inorganic–Organic Hybrid Nanostructured Solar Cells. *Nano Letters*2013: **13**; 1764–1769.

[135] Galasso FS, Smoluchowski R, Kurti N. Structure, Properties and Preparation of Perovskite-Type Compounds: International Series of Monographs in Solid State Physics: Elsevier Science; 2013.

[136] Chung I, Lee B, He J, Chang RPH, Kanatzidis MG. All-solid-state dye-sensitized solar cells with high efficiency. Nature. 2012;485:486-9.

[137] Dwivedi C, Dutta V, Chandiran AK, Nazeeruddin MK, Grätzel M. Anatase TiO2 Hollow Microspheres Fabricated by Continuous Spray Pyrolysis as a Scattering Layer in Dye-Sensitised Solar Cells. Energy Procedia. 2013;33:223-7.

[138] Liu D, Kelly TL. Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques. Nat Photon. 2014;8:133-8.

[139] Kumar MH, Yantara N, Dharani S, Graetzel M, Mhaisalkar S, Boix PP, et al. Flexible, low-temperature, solution processed ZnO-based perovskite solid state solar cells. Chemical Communications. 2013;49:11089-91.

[140] Eperon GE, Burlakov VM, Docampo P, Goriely A, Snaith HJ. Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells. Advanced Functional Materials. 2014;24:151-7.

[141] Burschka J, Pellet N, Moon S-J, Humphry-Baker R, Gao P, Nazeeruddin MK, et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. Nature. 2013;499:316-9.

[142] Lanzani G. The Photophysics behind Photovoltaics and Photonics: Wiley; 2012.

[143] Lai Y-H, Lin C-Y, Chen H-W, Chen J-G, Kung C-W, Vittal R, et al. Fabrication of a ZnO film with a mosaic structure for a high efficient dye-sensitized solar cell. Journal of Materials Chemistry. 2010;20:9379-85.

[144] Park N-G. Perovskite solar cells: an emerging photovoltaic technology. Materials Today. 2015;18:65-72.

[145] Frost JM, Butler KT, Walsh A. Molecular ferroelectric contributions to anomalous hysteresis in hybrid perovskite solar cells. Apl Materials. 2014;2:081506.

[146] Xia WS, Li LX, Ning PF, Liao QW. Relationship Between Bond Ionicity, Lattice Energy, and Microwave Dielectric Properties of Zn (Ta1– xNbx) 2O6 Ceramics. Journal of the American Ceramic Society. 2012;95:2587-92.

[147] Sanchez RS, Gonzalez-Pedro V, Lee J-W, Park N-G, Kang YS, Mora-Sero I, et al. Slow dynamic processes in lead halide perovskite solar cells. Characteristic times and hysteresis. The Journal of Physical Chemistry Letters. 2014;5:2357-63.

[148] Liang PW, Liao CY, Chueh CC, Zuo F, Williams ST, Xin XK, et al. Additive enhanced crystallization of solution-processed perovskite for highly efficient planar-heterojunction solar cells. Advanced Materials. 2014;26:3748-54.

[149] Xie FX, Zhang D, Su H, Ren X, Wong KS, Grätzel M, et al. Vacuum-Assisted Thermal Annealing of CH3NH3PbI3 for Highly Stable and Efficient Perovskite Solar Cells. ACS Nano. 2015;9:639-46.

[150] Eames C, Frost JM, Barnes PR, O'regan BC, Walsh A, Islam MS. Ionic transport in hybrid lead iodide perovskite solar cells. Nature communications. 2015;6.

[151] Niu G, Guo X, Wang L. Review of recent progress in chemical stability of perovskite solar cells. Journal of Materials Chemistry A. 2015;3:8970-80.

[152] Lee JW, Kim DH, Kim HS, Seo SW, Cho SM, Park NG. Formamidinium and Cesium Hybridization for Photo-and Moisture-Stable Perovskite Solar Cell. Advanced Energy Materials. 2015;5.

[153] Cappel UB, Daeneke T, Bach U. Oxygen-induced doping of spiro-MeOTAD in solid-state dye-sensitized solar cells and its impact on device performance. Nano Letters. 2012;12:4925-31.

[154] Ye S, Sun W, Li Y, Yan W, Peng H, Bian Z, et al. CuSCN-based inverted planar perovskite solar cell with an average PCE of 15.6%. Nano Letters. 2015.

[155] Christians JA, Fung RC, Kamat PV. An inorganic hole conductor for organo-lead halide perovskite solar cells. Improved hole conductivity with copper iodide. Journal of the American Chemical Society. 2013;136:758-64.

[156] Wang K-C, Jeng J-Y, Shen P-S, Chang Y-C, Diau EW-G, Tsai C-H, et al. p-Type mesoscopic nickel oxide/organometallic perovskite heterojunction solar cells. Scientific reports. 2014;4.