



# 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 sulfide (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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## 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

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rate of 1.5% per annum from 2010 to 2040 as shown in Fig. 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 year 2007–2050, 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 Fig. 2 and the growth rate for the photovoltaics (PV) industry is  $\sim 30\%$  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].

Today 80–90% of the solar cell technology is dominated by silicon-based materials [9], and silicon technology is the mainstream and proven to be a robust technology in the PV modules. The reason behind this is that 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 the following methods have been employed:

- Use of hydrogenated silicon [11].
- Use of nanoparticles 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

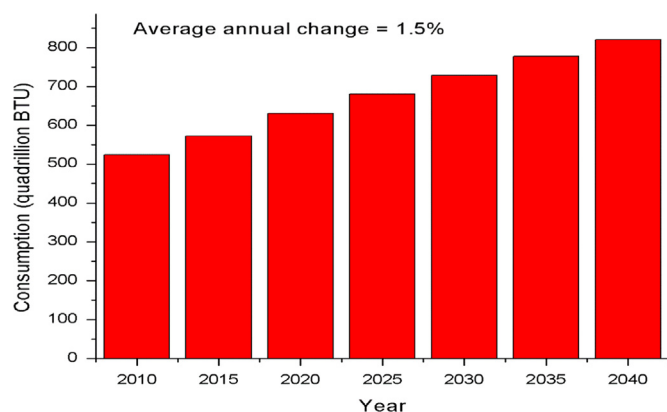


Fig. 1. World energy consumption, 2010–2040 (quadrillion BTU).

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  $\text{TiO}_2$  and ZnO and their nanostructures; composite material  $\text{CuO/ZnO}$ ,  $\text{CIS/TiO}_2$ , etc., homojunction materials, such as  $\text{Cu}_2\text{O}$ ; and perovskite based solar cells, etc.

Fig. 3 shows the efficiencies plot for the key materials published in the current review from 2010 onward. It can be inferred from the figure that quantum dot and perovskite solar cell efficiency increases significantly.

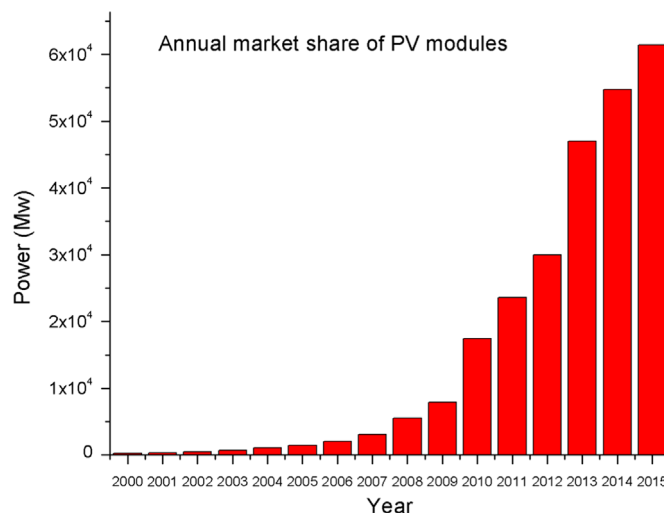


Fig. 2. Annual market share of PV modules.

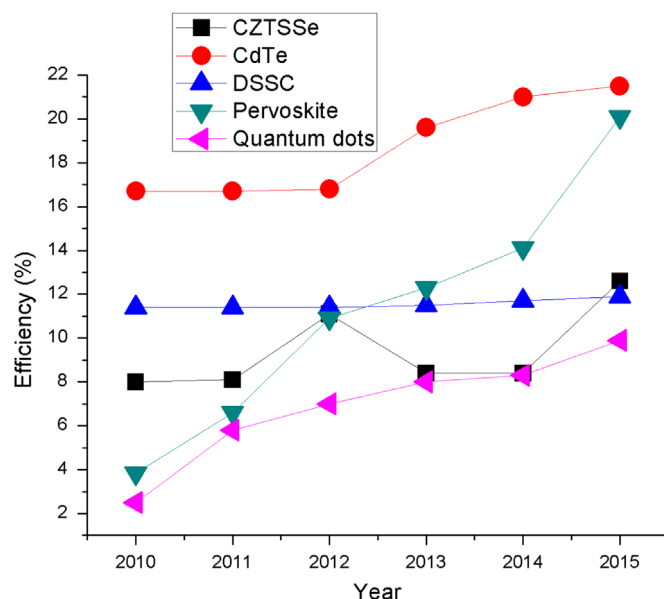


Fig. 3. Solar cell efficiency chart (2010–2015) [22–26].

## 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 [8]. The efficiency of the CdTe/CdS thin film solar cells was reported to be 22% [28]. 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 [29]. The photovoltaic performance of the CdTe solar cells depends 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 [30]. 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 [30–44].

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 ( $J_{sc}$ )  $\sim 27 \text{ mA cm}^{-2}$  can result in  $21 \pm 0.5\%$  efficient laboratory scale CdTe solar cell [8]. 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 [8]. 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 [46]. These effects cause the reduction in space charge width which increases the probability of light absorbance in the undepleted region [47].

Kim et al. [48] 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 [49]. For each gram of  $\text{CO}_2$  emission in the energy production from the grid, 0.03  $\mu\text{g}$  arsenic, 0.01  $\mu\text{g}$  of cadmium, 0.09  $\mu\text{g}$  of chromium, 0.1  $\mu\text{g}$  of lead (Pb) and 0.01  $\mu\text{g}$  of mercury (Hg) are emitted. Such emissions can be reduced by

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 [50].

### 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 [51]. The properties of quantum dots are size dependent with extraordinary tunable band gaps, high extinction coefficient, and most importantly multiple exciton generation [52]. It was reported that 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 [53].

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  $\text{TiO}_2$ ) and percolates in the wide band gap network and eventually reaches the conducting glass (an example is shown in Fig. 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 valence band of quantum dot and thus equilibrium is maintained [54]. Wang et al reported that multicrystalline Si solar cells with quantum dots are expected to have a maximum efficiency of 77% [55,56]. 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 [57]. 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 [58]. 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 [59].

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. [60] compared the relative toxicity of gold (Au) and carbon (C) nanoparticles with CdTe nanoparticles 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 nanoparticles, and then to carbon nanodots. Xiao et al. [61] 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.

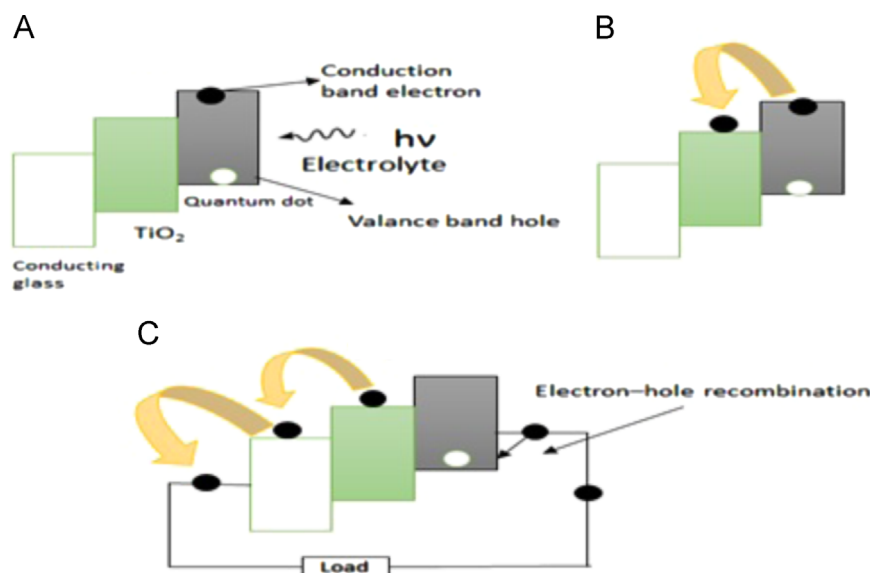
### 2.3. CZTS thin films

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. 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 extensive 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

**Table 1**

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

Superstrate configuration (laboratory scale)							Ref.
Method	Efficiency	$V_{oc}$ (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	Area	Substrate	
CSS	19.6%	857	28.6	80.0	1.04	Glass	[45]
VTD	19%	872	28.0	78.0	0.48	Glass	[40]
VTD	16.4%	835	23.8	82.5	0.36	Glass	[41]
Substrate configuration (laboratory scale)							Ref.
HVE	13.6%	852	21.2	75.3	0.3	Glass	
Commercial technology							Ref.
VTD	16.1%	68.7	2.25	74.8	0.72	N/A	

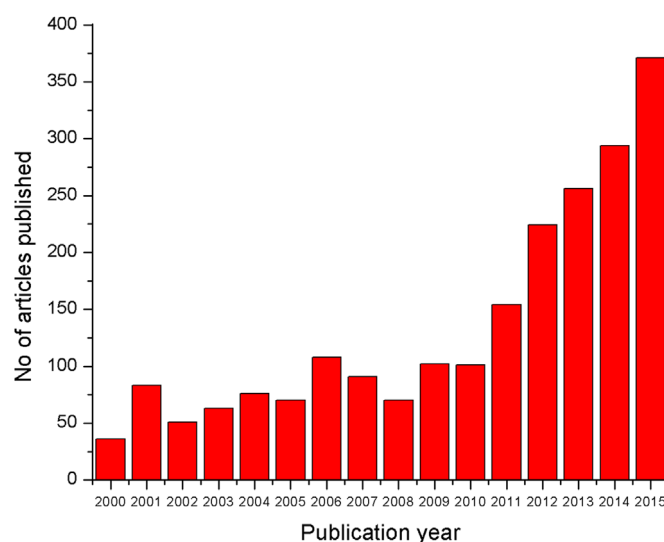


**Fig. 4.** Quantum dot solar cell (A) the electron is excited into the conduction band; (B) electron enters into the conduction band of  $\text{TiO}_2$ ; and (C) electron–hole recombination after passing through electrolytic solution.

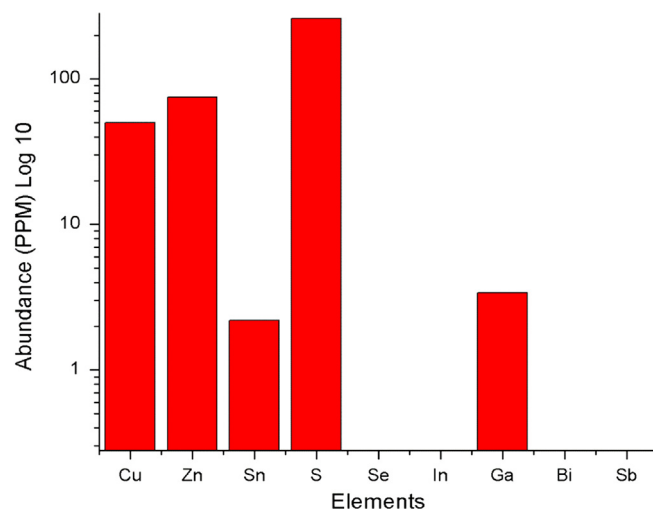
is only 2.86 meV per atom larger than that for the kesterite structure [62]. Optoelectronic and structural properties of both the CIGS and CZTS can be enhanced by replacing its constituent elements with earth abundant and nontoxic elements, such as  $\text{SnSbS}_4$  and  $\text{CuS}$ , etc. [63]. For the CZTS, the high absorption coefficient ( $10^4 \text{ cm}^{-1}$ ) and optimum band gap (1.0–1.5 eV) cover the maximum solar spectrum and open 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% [49,64].

CZTS has been synthesized using different techniques in the form of thin films and nanocrystal 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 [65,66]. 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 [67,68]. By optimizing the process parameters, the defects in the film can be reduced, which ultimately enhances 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 Fig. 5.

The abundance of different elements in earth crust used in the CZTS and CIGS solar cell materials as compared to others is shown in Fig. 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 Fig. 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 cells (CIGS) are



**Fig. 5.** Publication chart for CZTS (obtained from Elsevier 2000–2015).



**Fig. 6.** Abundance of different materials in earth crust [69,70].



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 [71,72].

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 [72]. 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 [73] 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 Fig. 8 [74–78]. The thinnest material used in thin film PV technology is CuInSe<sub>2</sub> while the thickest one is c-Si.

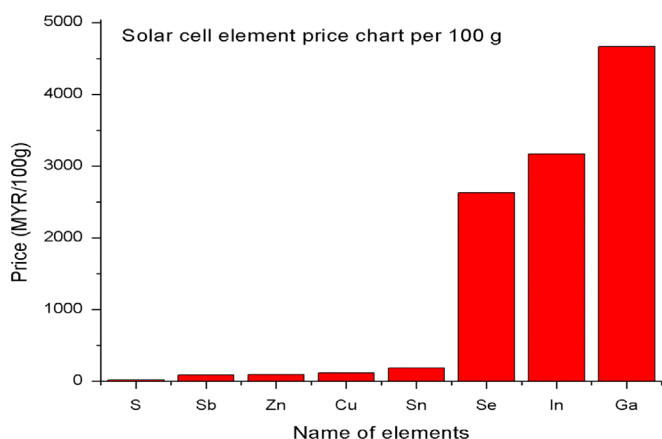


Fig. 7. Price chart for solar cell materials [http://www.lesker.com].

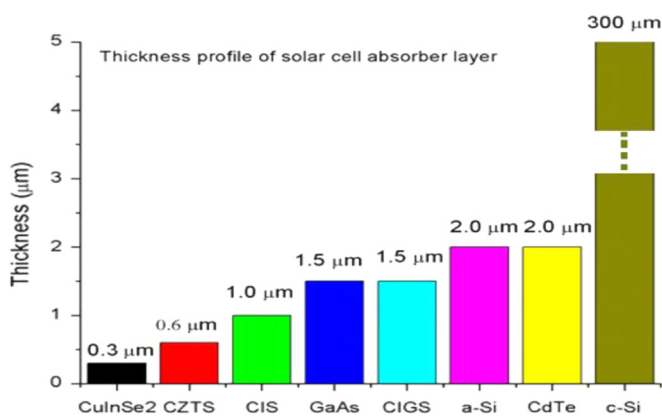


Fig. 8. General thickness profile of absorber layer (for most solar cells).

However, CuInSe<sub>2</sub> due to its usage of rare elements is not the preferred material in solar cell technology.

### 2.3.1. Tin antimony sulfide thin films

Tin antimony sulfide (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 [58]. Tin antimony sulfide has different phases such as SnSb<sub>2</sub>Se<sub>4</sub>, Sn<sub>3</sub>Sb<sub>2</sub>S<sub>5</sub>, Sn<sub>3</sub>Sb<sub>2</sub>S<sub>6</sub>, Sb<sub>2</sub>Sn<sub>5</sub>S<sub>9</sub>, SnSb<sub>2</sub>S<sub>4</sub>, Sn<sub>4</sub>Sb<sub>6</sub>S<sub>13</sub>, Sn<sub>6</sub>Sb<sub>10</sub>S<sub>21</sub>, etc. [65]. Gassoumi and Kanzari [79] 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. [80] 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 ( $10^5 \text{ cm}^{-1}$ ) was reported for this emerging material with a high photoconductivity in visible and near infrared region [80]. The effect of oxygen annealing on the properties of Sn–Sb–S thin films was studied by Fadhli et al. [81]. They reported that the extra phases of SnO<sub>2</sub> 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 [82]. 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) [83].

## 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 [84].

The main components of the DSSCs are dye sensitized photoanode, counter electrode and redox electrolyte. In photo-electrochemical systems, many semiconductor materials have been used as photoelectrodes, including single crystal and polycrystalline 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<sub>2</sub> and SnO<sub>2</sub> 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 [85]. Gong et al. [42] 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 [44].

Li et al. [44] 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 [44].

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, optical reflection, etc.

### 3.1. $\text{TiO}_2$ films and nanostructures

$\text{TiO}_2$  is used as thin film solid state DSSCs (SS-DSSCs) and nanostructured DSSCs. In the thin films SS-DSSC,  $\text{TiO}_2$  is normally deposited on conducting transparent glass as an electrode in the solar cell, generally using “doctor blading” method [86]. The dye molecules are attached to the surface of  $\text{TiO}_2$  particles by a chemical bond, i.e., or generally called sensitization. In nanostructured  $\text{TiO}_2$  DSSCs (nanoparticles, nanowires, nanotubes, nanorods),  $\text{TiO}_2$  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  $\text{TiO}_2$  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 [87].

SS-DSSCs show that their open circuit photovoltages ( $V_{oc}$ ) often exceed those of liquid 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 [88,89], or organic dyes [85], remains significantly below those of electrolyte-based devices. The smaller  $J_{sc}$  values arise from the fact that the SS-DSSC employs only 1.5–3  $\mu\text{m}$ -thick nanocrystalline  $\text{TiO}_2$  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  $\text{TiO}_2$  electrodes is advantageous [90].

Recent advances in the photovoltaic performance of the SS-DSSC have augmented the power conversion efficiencies from the initial 0.74% [91], to in the range of about 5–7% [92–95]. Recently this maximum value was reported to be 15% for the SS-DSSC.

Liu et al. [96] 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  $\mu\text{m}$  thick layer of  $\text{TiO}_2$  as a dense layer to control short circuiting and nanoscale thin film as electrode. The calcination was carried out at 500  $^\circ\text{C}$  and a cell was obtained with enhanced properties of  $V_{oc}$ ,  $J_{sc}$ , FF and efficiency values of 880 mV, 8.22  $\text{mA}/\text{cm}^2$ , 0.44, and 3.21%, respectively. Xue et al. [97,98] recently studied the properties of  $\text{TiO}_2$  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  $\text{mA}/\text{cm}^2$  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. [99] reported the synthesis of proliferous  $\text{TiO}_2$  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  $\text{TiO}_2$  nanoparticle 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  $\text{TiO}_2$  between FTO and electrolyte [100]. Sangiorgi et al. [101] 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  $\text{TiO}_2$ , ZnO, Au, graphene oxide and  $\text{Nb}_2\text{O}_5$  layers were also reported as blocking layers by a number of groups. Liu et al. [102] reported the effect of all blocking layers on the properties of DSSC and reported that ZnO is advantageous over  $\text{TiO}_2$  and other layers. The thickness of the blocking layer must not exceed 300 nm in order to prevent the blocking layer from charge trap [102].

The introduction of foreign dopant in  $\text{TiO}_2$  was also reported for enhancing the properties of the DSSC device [103]. The effect of doping Zn on  $\text{TiO}_2$  was studied by Niaki et al. [104] and stated that  $\text{Zn}^{2+}$  has lower numbers of valence electrons than those of  $\text{TiO}_2^{4+}$ , therefore, excess of holes is created by generating an acceptor band near  $\text{TiO}_2$  valence band which helps in migration of electrons between bands.

Kuang et al. [105] reported that the length of  $\text{TiO}_2$  nanotubes influences the properties of the DSSCs, and they studied 5–14  $\mu\text{m}$  long nanotube arrays whose length was controlled by the anodization duration. The nanotubes reduce the adsorption of dyes on  $\text{TiO}_2$  surface due to decrease in the surface area which reduces the properties of the DSSCs. Yang et al. [106] reported the treatment of  $\text{TiCl}_4$  on  $\text{TiO}_2$  nanotubes (TNT) to overcome this problem. The study was also carried out for a composite film of TNT (10 wt%) and  $\text{TiO}_2$  nanoparticles dipped for 30 min in 60 mM solution of  $\text{TiCl}_4$  at 70  $^\circ\text{C}$  for 30 min and annealed at 450  $^\circ\text{C}$  for 15 min.

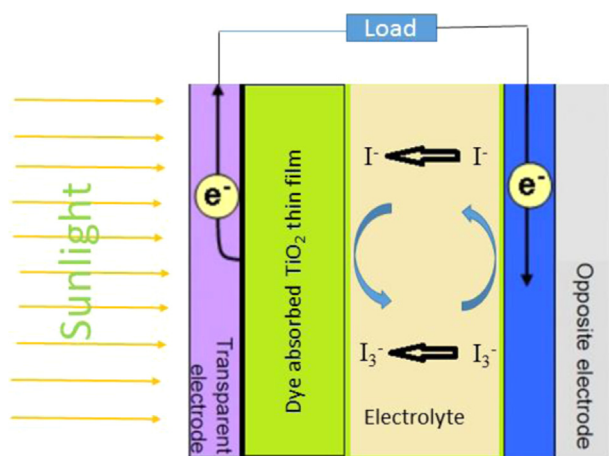


Fig. 9. Schematic of  $\text{TiO}_2$  based dye sensitized solar cell.

Mathews et al. [107] recently reported the DSSCs with an efficiency of 13% by engineering the structure of  $\text{TiO}_2$ . In nanostructured materials, the nanoparticles of  $\text{TiO}_2$  are predominant in achieving a maximum efficiency attributing to the large surface area of nanoparticles. 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 [108].

### 3.2. ZnO nanowires

Nanostructured zinc oxide is recently used as a multi-function material in solar cells. ZnO has a wide band gap with higher bulk electron mobility than  $\text{TiO}_2$  which can overcome a high electron recombination. However, the efficiency of nanostructured ZnO based devices is lower than that of the  $\text{TiO}_2$ , and few studies on ZnO nanostructured DSSC solar cells have achieved a high conversion efficiency [109]. Martinson reported that the surface morphologies of ZnO are more amenable in comparison to  $\text{TiO}_2$  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 [110–115]. 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 [115]. Cheng et al. [115] reported the synthesis of ZnO nanowires using a modified aqueous solution method for the DSSC on seeded fluorine-doped tin oxide (FTO) substrates. The nanowires were coated with the ZnO nanoparticles by dip coating techniques followed by the growth of branched ZnO nanowires. The DSSCs using standard nanowire were also studied in comparison with the branched ZnO nanowires DSSC.

Choi et al. [116] 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. [110]. Hsu and Chang [117] reported that Ag doped ZnO nanorods grown on stainless steel (SS) mesh were efficient visible-light photo-catalysts with high activity and stability. Ag doped ZnO nanorods not only increased the surface area of photocatalysts but also enhanced red-shift in the absorption band and improved the visible light absorption capacity [117]. Chae et al. [118] 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 nanorods which ultimately affected the solar cell parameters. The ideal dye loading time was optimized to be two hours [119] which leads to an efficiency of 2.57%.

Gondoni et al. [120] 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 [119]. 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 [121] ZnO nanowires with an average length of 6  $\mu\text{m}$  and diameter of 100 nm and ZnO nanoparticles 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. [122] 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. [123] using hierarchical structure nanowires and nano-sheet photo-anode. The maximum efficiency for ZnO nanostructured (5.41%) reported by Lin et al. [124] 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  $\text{Zn}^{2+}$ /dye complex. Core-shell structured  $\text{TiO}_2$ -ZnO nanostructures have been considered as promising candidates to solve this problem. With  $\text{TiO}_2$  shell, the electron injection efficiency can be maintained at normal level for most of commonly used dye. Additionally, by applying  $\text{TiO}_2$  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 [125,126].

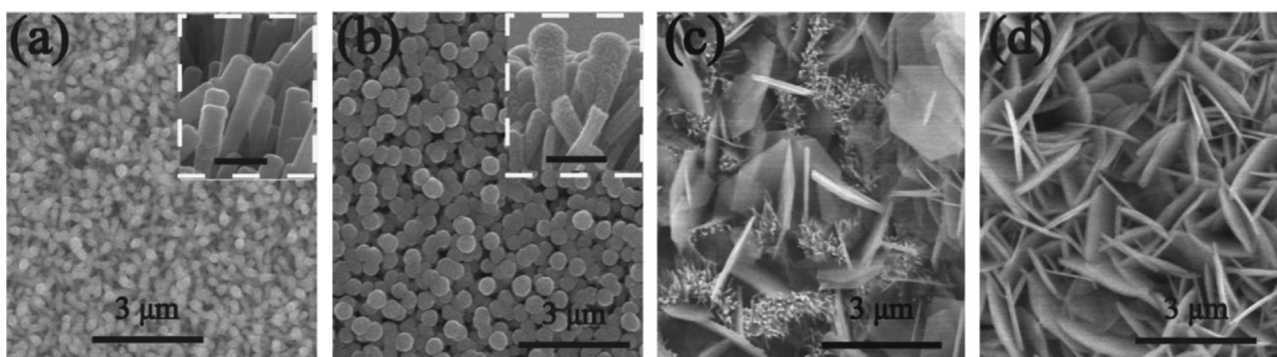
Chao et al. [127] recently used two sequential low-temperature processes to achieve a core-shell structure. To reduce the process temperature, combination of hydrothermal growth of ZnO and plasma ion assisted evaporation of crystalline  $\text{TiO}_2$  shell was employed. By adjusting deposition parameters, ZnO nanorods can be homogeneously covered with a layer of anatase  $\text{TiO}_2$  nanostructure to form core-shell nanorods and nano-sculptured foxtail-like patterns (in Fig. 10(a) and (b)). Power conversion efficiency of DSSCs was improved from 0.3% to 1.8% after using the ZnO/ $\text{TiO}_2$  hybrid structure due to reduced recombination as well as improved 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/ $\text{TiO}_2$  to Al doped ZnO/ $\text{TiO}_2$  nanostructures (see Fig. 10(c) and (d)) with highest average PCE of 4.5% were achieved. [128] 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 improving the power conversion efficiency.

## 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 [100,129]. However, concern over leakage of the liquid electrolyte has caused a bottleneck in rapid development and commercialization; therefore, there is need for new designs of solid-state sensitized solar cells to replace the liquid electrolyte with hole-transporting material (HTM). Currently

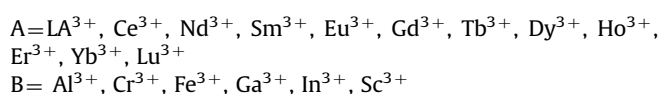




**Fig. 10.** Represented SEM images of the as synthesized ZnO/TiO<sub>2</sub> hybrid (a) nanorods, (b) foxtail-like nanostructure; and (c) hybrid nanostructure composite Al doped ZnO nanoflakes with ZnO nanorods. (d) Al doped ZnO nanoflakes.

molecular HTM of 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiroMeOTAD) is 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<sub>2</sub> 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<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> having a perovskite structure. The reported photo-to-electron conversion efficiency (PCE) for mesoporous TiO<sub>2</sub> film adsorbed with perovskite CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> nanocrystals was 9.7% under AM1.5 illumination in 2012 [130]. 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 photovoltaics with over 20.1% conversion efficiency [131].

The general stoichiometry of the perovskite structure consists of ABX<sub>3</sub>, where "A" and "B" are cations and X is anion. A and B consist of the following elements such that A is larger than B [132,133].



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<sub>3</sub> perovskite as solid state DSSC with 8.5% efficiency was reported by Chung et al. [133] soon after the discovery of the perovskite in photovoltaics. In the same year, another group reported efficiency of 8.0% using perovskite methylammonium lead iodide chloride (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>2</sub>Cl) as light absorber and TiO<sub>2</sub> as a transparent n-type counterpart. The same group reported 11% efficiency by replacing the photo-electrode (TiO<sub>2</sub>) by an insulating Al<sub>2</sub>O<sub>3</sub> in combination with perovskite material [134]. The use of thin film configuration of the perovskite solar cell was introduced to deposit the film directly on TiO<sub>2</sub> compact layer in order to avoid any mesoporous layer. Liu et al. [135] used vapor deposited perovskite film onto TiO<sub>2</sub> films and reported an efficiency of 15.4%. Kumar et al. [136] employed two different approaches for the deposition of ZnO as a blocking layer on FTO and ITO coated substrates. The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> 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 were utilized in the assembly of planar solar cell based on ITO

and FTO substrate. 15.7% and 10.2% efficiencies were recorded or the perovskite devices on the FTO and ITO substrates respectively [135,137]. Burschka et al. [138] reported 15% efficiency for perovskite sensitized hybrid solar cell employing two different techniques, spin coating and sequential deposition on mesoporous TiO<sub>2</sub>. 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 [130,139]. Seok's group in 2013 reported 16.2% efficiency for perovskite solar cell by using CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Br<sub>x</sub> (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 [139,140].

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% [141,142]. Recently, slightly over 20% efficiency was claimed to be achieved with a solid state CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> based solar cell device [143]. The organometallic halide perovskite absorbers have better properties than metal chalcogenide quantum dots, though they have the same absorption coefficient [117,133].

#### 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 paraelectric or ferroelectric properties of perovskites at room temperature and above [144,145]. 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 [144]. However, others would suggest that, because of its low lattice energy, organometal halide perovskite tends to possess strong ionic characteristics, which is sensitive to polarization in an electric field [145]. Impedance study shows that a high value of the dielectric constant at low frequencies resulting from a combination of dipolar, ionic and electronic contributions is the main reason for the *J/V* hysteresis [146].

In general, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> crystals are prepared using solution process via one-step or two-step, depending on whether the precursor solution (PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I) is 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  $\text{CH}_3\text{NH}_3\text{PbI}_3$  seed clusters [147], whereas with the sequential deposition method it is hard to ensure purity of the resultant  $\text{CH}_3\text{NH}_3\text{PbI}_3$  as the residual organic component introduces a poor stability [148]. Finally, good crystallite characteristics of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  are 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  $\text{CH}_3\text{NH}_3\text{PbI}_3$  [149].

The stability of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  films also depends significantly on a variety of environmental factors including temperature, radiation, oxygen and moisture [150]. 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  $\text{CH}_3\text{NH}_3\text{PbI}_3$  has an intrinsic nature of thermal instability [151]. Thermo-gravimetric analysis and chemical analysis results indicated that  $\text{CH}_3\text{NH}_3\text{PbI}_3$  suffers from an irreversible photo-degradation and a subsequent loss of organic cation component even in the absence of oxygen and moisture with temperature higher than  $85^\circ$  [151].

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  $\text{CH}_3\text{NH}_3\text{PbI}_3$  [152]. As a result, tremendous efforts have been focused on replacing spiro-OMeTAD. Besides organic molecule HTMs, inorganic materials such as  $\text{CuSCN}$  [153],  $\text{CuI}$  [157], and  $\text{NiO}$  [158] have also been employed to serve as low cost hole extraction materials with long-term stability indicating practical potential. Among them,  $\text{NiO}$  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 doctor 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 commercialized thin film based solar cells.

- The selenization of the CZTS film is promising 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 dye-sensitized 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,  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , 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 being 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.

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