A brief review of ZnO based Perovskite Solar Cells and its future trends

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Abstract

Perovskite Solar Cells (PSCs) have risen as brightest star in the sky of solar cells with increase in efficiency up to 25%. The inimitable characteristics of perovskite materials e.g. high absorption over the visible region and longish distance before diffusion have been attributed for astonishing performance of perovskite solar cells. Because of the unlike diffusion lengths of holes and electrons, electron transporting layers (ETLs) plays a key role in performance of the perovskite solar cells. TiO_2 is the materials, which have been used for ETLs in most frequently testified PSCs. The physical properties of ZnO materials are comparable with that of TiO_2 but mobility of electrons in ZnO is much higher than TiO_2, Which make it a better option than TiO_2. Other than this, there are many simple techniques which have lower cost and consume lesser energy, can be used for the fabrication of ZnO nanomaterials. This review is focused on current advances in the ZnO based ETLs for PSCs and impact of different kinds of ZnO ETLs on the performance of PSCs.Influence of different ZnO nanostructure, deposition and post treatment techniques and doping in ZnO on the performance of PSCs have been discussed. The challenges faced in using ZnO ETLs and solutions to these challenges are also discoursed.

Keywords: ZnO; Perovskite solar cells; Electron Transport Layer; ZnO nano structures; deposition and post treatment technique, doping.

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1. Introduction

The human advancement is marching frontward but it is escorted by an imminent energy scarcity. To acquire clean and inexhaustible energy is still a significant issue that has to be resolved. Amongst all the renewable energy sources the solar energy is copious and less reliant on the geographical locations. Solar energy technologies have boomed in current years and the production cost has been remarkably reduced with the advancement of solar cells from 1st generation to 3rd generation. Perovskite solar cell technology has risen like a star in recent years owe to its easy and low cost production techniques with high energy conversion efficiency. PSCs have attained a certified energy conversion efficiency of around 23.3% on inflexible conductive substrates [1] and around 19.5% on substrates that are flexible [2]. The inimitable features of perovskite materials, for example high visible range absorption, long span for diffusion and high charge mobility have been attributed for marvelous performance of perovskite solar cells [3-6]. An important advantage of PSCs over other thin-film based photovoltaic cells is the easy availability of the precursors. Other types of 3rd generation photovoltaic devices are still struggling with the issues of intricate fabrication techniques or relatively low conversion efficiencies, which make their commercialization to be very difficult. Hence, PSCs could be an inspiring aspirant for the next generation photovoltaic technologies in terms of fabrication cost as well as efficiency [7]. In this paper, current advances in the use of ZnO ETLs and the factors affecting the performance of ZnO-based PSCs are discussed systematically.

2. Perovskite Solar Cells (PSCs)

Perovskite structure is something which has the generic formula ABX_3, where A represents an organic cation like methylammonium ($CH_3NH_3^+$) or formamidinium ($NH_2CHNH_2^+$), B represents a big inorganic cation usually lead (Pb^{2+}) and X_3 represents a somewhat smaller halogen anion such as chloride (Cl^-) or iodide (I^-). The perovskite lattice arrangement has been demonstrated below in Fig 1.(a).The perovskite materials have the following features which make them advantageous for the solar cell applications:

- The perovskite materials possess outstanding photoelectric properties, high optical absorption coefficients and lower binding energy of excitons [8].
- A perovskite material based light absorbing layer can engross sun light proficiently [9].
- These materials possess large dielectric constant and transmit and collect the charge carriers efficiently [10].
- The holes and electrons in the perovskite materials can be simultaneously transmitted up to transmission distance of 100 nm or more [11–13].

The special features of the perovskite materials actually lead to a high open-circuit voltage and a short-circuit current density of the solar cell devices. Normally, the PSCs comprise an absorber layer inserted between ETL and HTL. When the absorber layer of perovskite material is exposed to sun light, it absorbs photons and yield excitons and because of the difference in the binding energy of the excitons, free charge carriers can be easily produced for the generation of current or they can recombine. The low probability of recombination and higher mobility of charge carriers in perovskite layer, leads to the longer length of diffusion and life span of the charge carrier [14, 15], which results in outstanding performance of PSCs. After that these free charge carriers are collected by an ETL and HTL. Electrons are migrated from the perovskite absorbing layer to ETL and finally collected by cathode and at the same time, the holes are moved to the HTL and diffuses to the direction of counter-electrodes. Finally, the holes and electrons recombine and photocurrent is produced in the outer circuit.

The first attempt to fabricate PSC was made in 2009 by Kojima and colleagues [16]. After that, many scientists studied the advancement of $CH_3NH_3PbI_3$ based PSCs. Their conversion efficiency observed to be increase from 3.8%- 20.7 % for time span of less than ten years [17].

3. Role of ETL in PSCs

Generally there are two basic designs for the PSCs that are mesoporous and planar, with further subtypes- n-i-p and p-i-n as shown in Fig 1 (b)-(e). ETL is actually a layer that averts the holes to reach the transparent conducting oxide electrode[18]. ETLs should satisfy the following conditions:

(i) To cut down the optical energy losses, ETLs should have good transmittance in the visible region.
(ii) For good electron extraction and to block the holes in an efficient way, the energy levels of ETLs should comparable with that of perovskite materials .
(iii) It should have high mobility of electrons;
(iv) It should be easy to fabricate a ETL film of high quality, so that its design and materials characteristics can be suitable to achieve an efficient solar cell [14, 19, 20].

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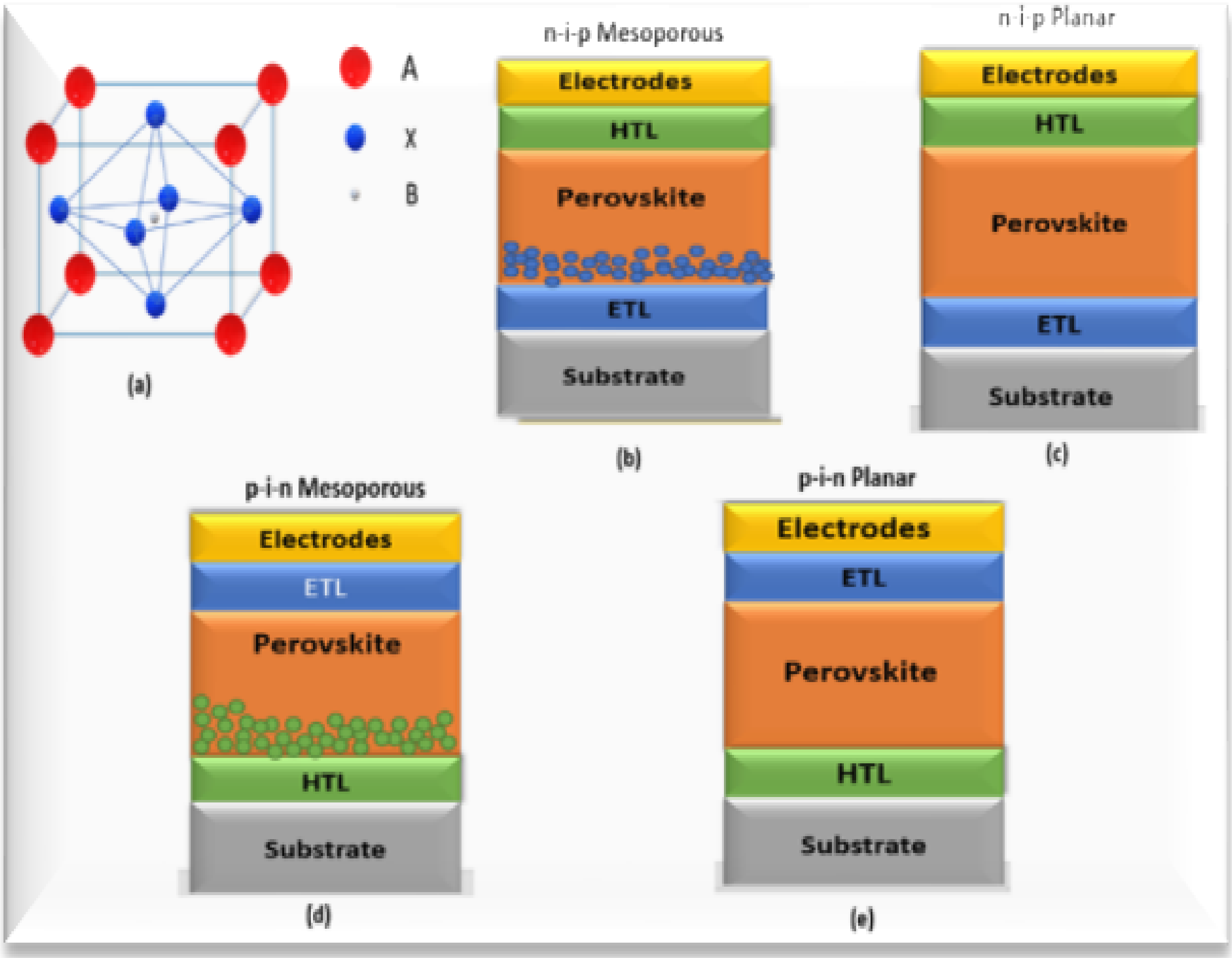

Fig.1 (a) Perovskite crystal structure, (b)-(e) Distinctive structures of PSCs

The carrier mobility, alignment of energy band, morphology, trap states and interfacial properties of the ETLs are chief factors which are actually accountable for the behavior and performance of perovskite solar technology. To achieve high performance PSCs, the presence of ETL is essential. Many researchers have claimed to obtain the energy conversion efficiency of more than 13% for ETL free PSCs, but the incorporation of ETL in perovskite solar cells is still overriding in terms of efficiency and stability of the solar cells. J.Perez and other colleagues [21] investigated the performance of PSCs with ETL and without ETL in their research . They concluded that the absence of ETL has minor influence on the open-circuit voltage but have severely reduced short-circuit current density and fill factor, which have subsequent effect on the efficiency of the device. The incorporation of ETLs in PSCs has significantly increased the electron-hole recombination resistance at the cost of slight addition to the series resistance. Zhang and his colleagues [22] have also observed a drop of 2.7% from its maximum efficiency of 14.2% upon elimination of ETL from the device. They also examined that planar perovskite solar cell without ETL and observed that the energy conversion efficiency realized from current voltage measurement was relatively high and there was no sign of stabilized power output. Ke. et al. observed that the efficiency of PSC without ETL could range up to 14.1% but the device incorporating ETL has exhibited greater conversion efficiency of 16.1% [23]. There are several stable and outstanding metal oxides that can be used as ETLs in PSCs, such as TiO_2 [24-26], ZnO [27,28] and SnO_2 [29]. Amongst all above mentioned metal oxides,

TiO_2 nanostructure based films have been extensively used for ETLs in PSCs. The fabrication of films of TiO_2 necessitates high annealing temperatures (~500 °C) [14], which increases the energy payback time and would hamper the advancement of PSCs with flexible substrates. Thus, the fabrication and processing at low-temperature is significant for the research and advancement of solar cells. The energy band structure and physical properties of ZnO are comparable with TiO_2 (Table I), thus it can be a practical alternative for TiO_2 to design a PSCs with high efficiencies. Furthermore, ZnO can be synthesized easily by solution-processed techniques at low temperatures. N. A. Sultana et al. has studied that efficiency of the solar cell can be enhanced and expenses can be reduced if TiO_2 is replaced with ZnO [30]. Many investigations on ZnO-based PSCs have observed high energy conversion efficiencies and have delivered many new concepts. D. Y. Son et al. during their research compared the external quantum efficiency spectral response between ZnO nanorods and TiO_2 nanorods and observed the effectiveness of ZnO nanorods based ETLs in $CH_3NH_3PbI_3$ based PSCs [28]. SnO_2 is observed as a dynamic candidate to be used as an ETL in PSCs, because of its outstanding optical and electrical properties. E. Karimi et al. have investigated that using ZnO instead of SnO_2 will not only save manufacture expenses, but also enhance the solar cells efficiency for 22% [31].

4. ZnO based ETLs for PSCs

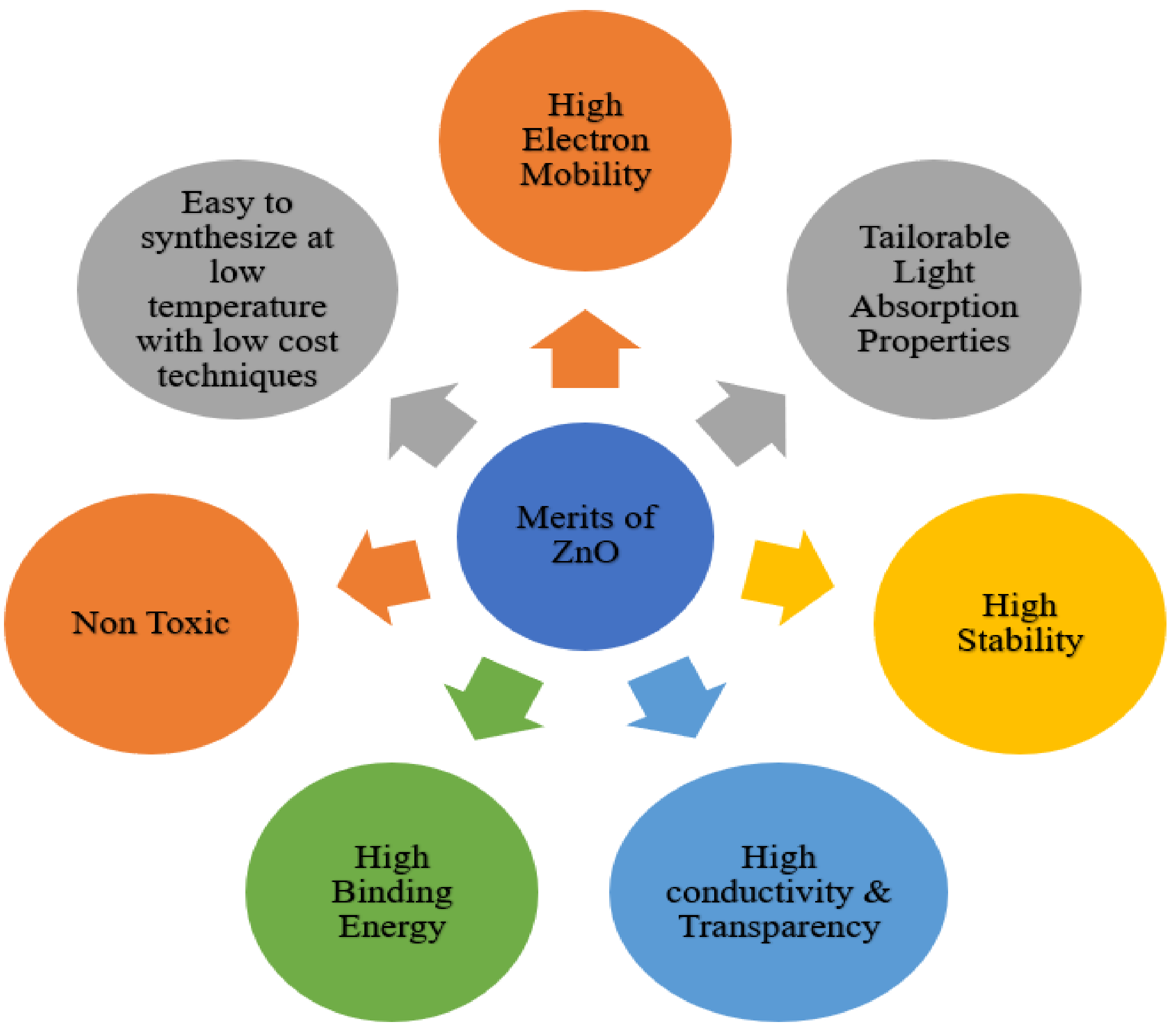

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Fig. 2 Merits of ZnO material

ZnO is a binary compound semiconductor belongs to II-VI group, which have excellent characteristics including good conductivity, high electron affinity, high stability and high mobility of electrons [32-34]. The features of ZnO have been shown in Fig. 2. These properties make it active for the solar devices. ZnO have wide energy bandgap (3.1–3.3 eV) at room temperature condition and can absorb light in the range of UV. Furthermore, if it is made to associate with other materials having smaller energy gaps e.g. organic polymers, then it can enhance their optical absorption.

It has been studied that, the bulk ZnO have an exciton Bohr radius of 2.35 nm [35]. It is comparable to the important confinement effects, detected through experimentation for the solution processed ZnO particles (particle radii of less than ~4 nm), because of the comparatively small effective masses for ZnO [36]. The high mobility of electrons in ZnO has made it fascinated for many solar cell applications, these values are comparatively better than TiO_2 [37] (Table I). ZnO has been recognized as a polymorph as it can have different morphologies depending on fabrication techniques. ZnO nanomaterials can have various shapes and structures such as nanocrystals, nanorods, nanospheres, nanowires, nanotubes, nanoflower and 3-D nanostructures. These outstanding traits of ZnO have made it appropriate for many technologies for example photodetectors, sensors, porous ceramics, supercapacitors and surface coating in addition solar cell devices.

	Zinc Oxide (ZnO)	**Titanium Oxide (TiO_2)**
Molecular Weight (g/mole)	81.38	79.866
Crystal structure	Cubic rock salt, Cubic zinc Blende, Hexagonal wurtzite	Anatase, Rutile, Brookite
Refractive Index	2.0034	2.488 (anatase), 2.609 (rutile), 2.583 (brookite)
Energy band gap (eV)	3.37	3.2
Surface work function (eV)	4.4 - 5.4	4.5 - 5.1
Electron Mobility ($cm^2V^{-1}s^{-1}$)	Bulk ZnO: 205 - 300 ZnO nanowire:1000	0.1 - 4.0
Effective mass of electrons (m_e)	0.23	9
Relative dielectric constant	8.17 – 9.34	172
Diffusion coefficient (cm^2s^{-1})	Bulk ZnO: 5.2 ZnO Nanoparticle film: $1.7x10^{-4}$	Bulk TiO_2: 0.5 TiO_2 Nanoparticles:10^{-8}–10^{-4}

Table I Comparison of different traits of ZnO with TiO_2.

One of the most important problems for the fabrication and better understanding of ZnO-based devices is doping, which essentially includes the heavy doping with trivalent elements of group III. Minami observed that aluminum and gallium doped ZnO semiconductors are appropriate to replace ITO for the application of thin-film transparent electrode[38].

Considering the important role of ZnO as ETLs in the performance of PSCs, study of the features of ZnO as the ETL, specifically its energy level alignment, morphology, trap states and interfacial characteristics, is very essential.

4.1. Different ZnO nanostructure for the performance of PSCs

Different nanostructures of ZnO have a noteworthy influence on the performance of PSCs. S.Yun et al. designed a configurable mesoporous structure that uses ZnO nanorod arrays with different lengths to improve the efficiency as well as stability of PSCs. It was observed that, ZnO nanorods with a suitable length could improve the infiltrate process of PSCs. This results in improved crystalline quality of the deposited film and also inhibit the charge recombination proficiently. They observed the maximum energy conversion efficiency with a length ~400 nm and with this the defect density, crystal size of perovskite and electron transfer distance got an optimal balance [39]. D.Y. Son et al. [24] prepared a PSC based on ZnO nanorods and investigated its performance of over 11%. K. Mahmood et al. [40] used a simple hydrothermal fabrication technique and fabricated the double-layer ZnO nanostructures with nanosheet arrays at the lowermost, adorned with horizontal nanorods. The better performance of PSCs was observed with increase in the ZnO nanorod density in the overlayer up to 10.35% and long term photostability even after a time span of 240 hrs. Y. Shirahata et al. [41] fabricated ZnO nanorods/perovskite solar cells using ZnO nanorods of different lengths. They produced the ZnO nanorods by using chemical bath deposition technique and developed hexagon-shaped nanorods. During the fabrication the lengths of the ZnO nanorods were controlled by monitoring carefully the deposition condition of ZnO seed layer. Solar cell properties of the ZnO nanorods/$CH_3NH_3PbI_3$ solar devices were examined by measurement of current density-voltage characteristics and energy conversion efficiency and the maximum conversion efficiency was observed for the lengthiest ZnO nanorods. A. Bahtiar et al. [42] efficaciously topped ZnO nanoparticles by reduced graphene oxide (rGO) using technique of electrophoretic. The stability of perovskite layer can be improvised significantly when it is deposited on ZnO-NPs/rGO layer by perceiving nonappearance of color transformation of perovskite after storing for 5 days in air with comparative moisture above 95%. They observed that by overlaying ZnO film with rGO, the efficiency as well as stability of perovskite solar cells can be modified remarkably.

4.2. Impact of different deposition methods and post-treatment techniques for ZnO ETL on the performance of PSCs.

The deposition methods and post-treatments affect the efficiency and stability of PSCs significantly with ZnO ETLs. The interaction between the perovskite and ETLs may be influenced by using varying processing techniques and which will affect the overall power conversion efficiency of the PSCs. Zheng with colleagues created the ZnO nano particles with spin coater, which caused in less energy conversion efficiency. The development of a pinhole-surface results the imperfect interface and leads to a loss of carriers [43].With the application of post treatment technique on prepared ZnO nanoparticles, the conversion efficiency of the PSCs could be enhanced.Academically, nanorods by providing a direct electron pathway with its 1-dim structure can lead to expand the conversion efficiency of PSCs. T. Jiang fabricated the PSCs with bilayer ETLs and tried to connect the benefits of effective charge extraction capabilities of $PC_{61}BM$ and outstanding hole blocking capabilities of ZnO nanoparticles against water, oxygen and electrode. Finally, they achieved the device with energy conversion efficiency as high as 17.2% and that too with high stability [44].

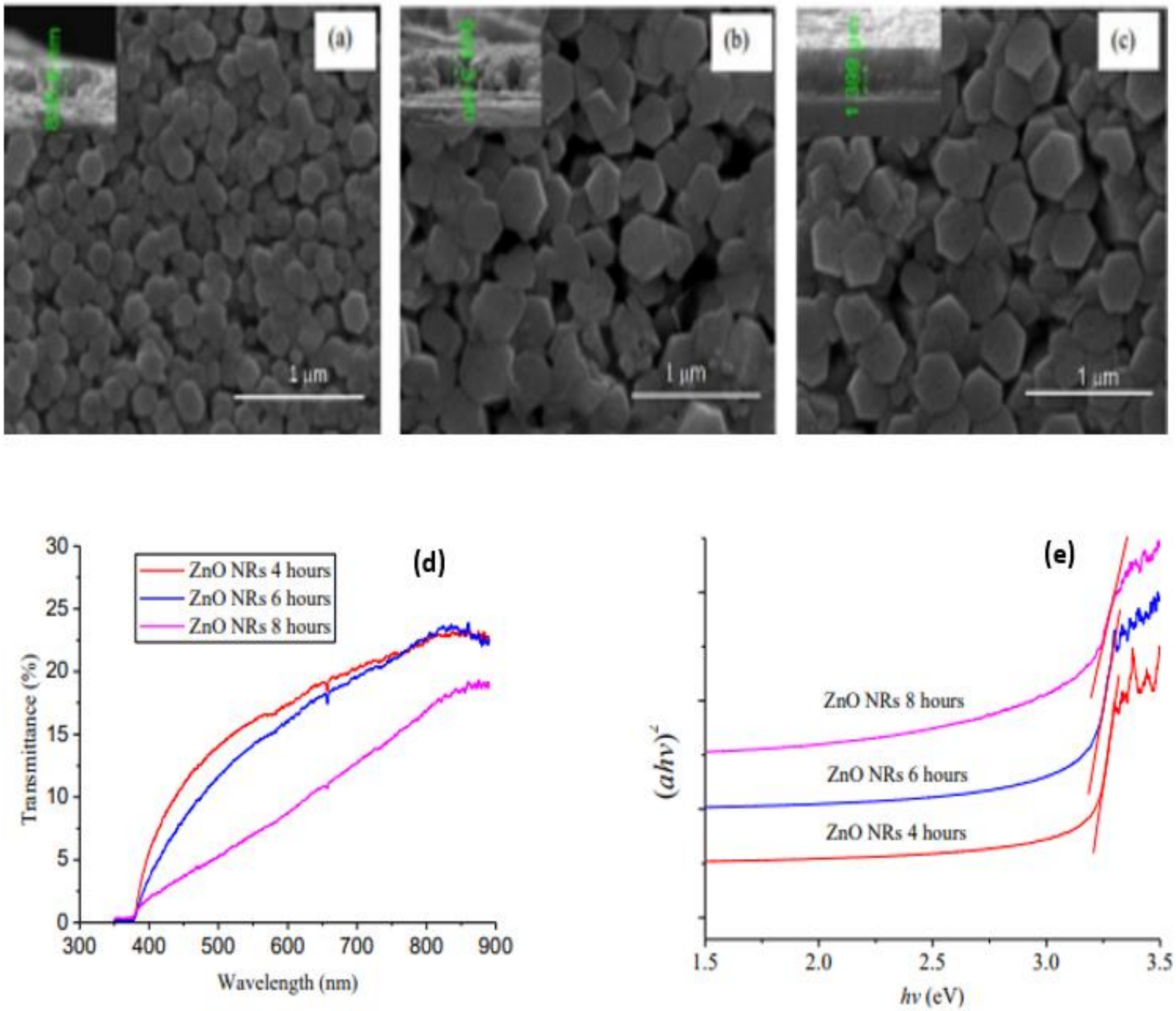

Fig. 3: SEM image of the ZnO nanorods grown with different growing times (a) 4 hrs., (b) 6 hrs., and (c) 8 hrs. (d) UV-Vis spectra for different growing time of ZnO nanorods. (e) Touch graph of ZnO nanorods for different growing times. Reproduced with permission [45].

Samples with different growing time (Hrs.)	Length (nm)	Diameter (nm)	Energy Bandgap (eV)
ZnO seed layer	---	---	3.216
ZnO nanorods, 4	835	138	3.145
ZnO nanorods, 6	934	230	3.120
ZnO nanorods, 8	1399	234	3.049

Table II: Dimensions of ZnO nanorods on different growing time. Data reproduced with permission [45]

N. Mufti et al. [45] (Figure 3) synthesized ZnO nano rods successfully using a hydrothermal technique. They observed that longer growing time results in ZnO nanorods with the bigger diameter and longer rod length (Table II). Beside this, they also observed the increased homogeneity and density of the fabricated ZnO nanorods and reduction in bandgap with the growing time. As each rod maintained each

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other in such a way that they lessened the likelihood of the nanorods to be distorted or inclined, thus the resulted denser structure of ZnO nanorods boost the orientation degree of nanorods to a vertical direction. Since ZnO nanorods film has a broader area relative to ZnO seed layer film, this makes the bandgap of ZnO nanorods smaller in comparison to the seed layer.

Y. Miao et al. [46] fabricated ZnO nano particles defect free thin films to be used as the ETL in PSCs fabricated at low temperature and without annealing. To achieve this, they treated the as-spun wet ZnO thin films with ultrasonic vibration at optimum conditions. The application of ultrasonic vibrations improved bridging among the ZnO nanoparticles and this improved about all the characteristics of the ZnO films amazingly. The treatment of ZnO based thin films with the ultrasonic vibration showed the best device efficiency of 11.3% as equated to 7.9 % for the control device.

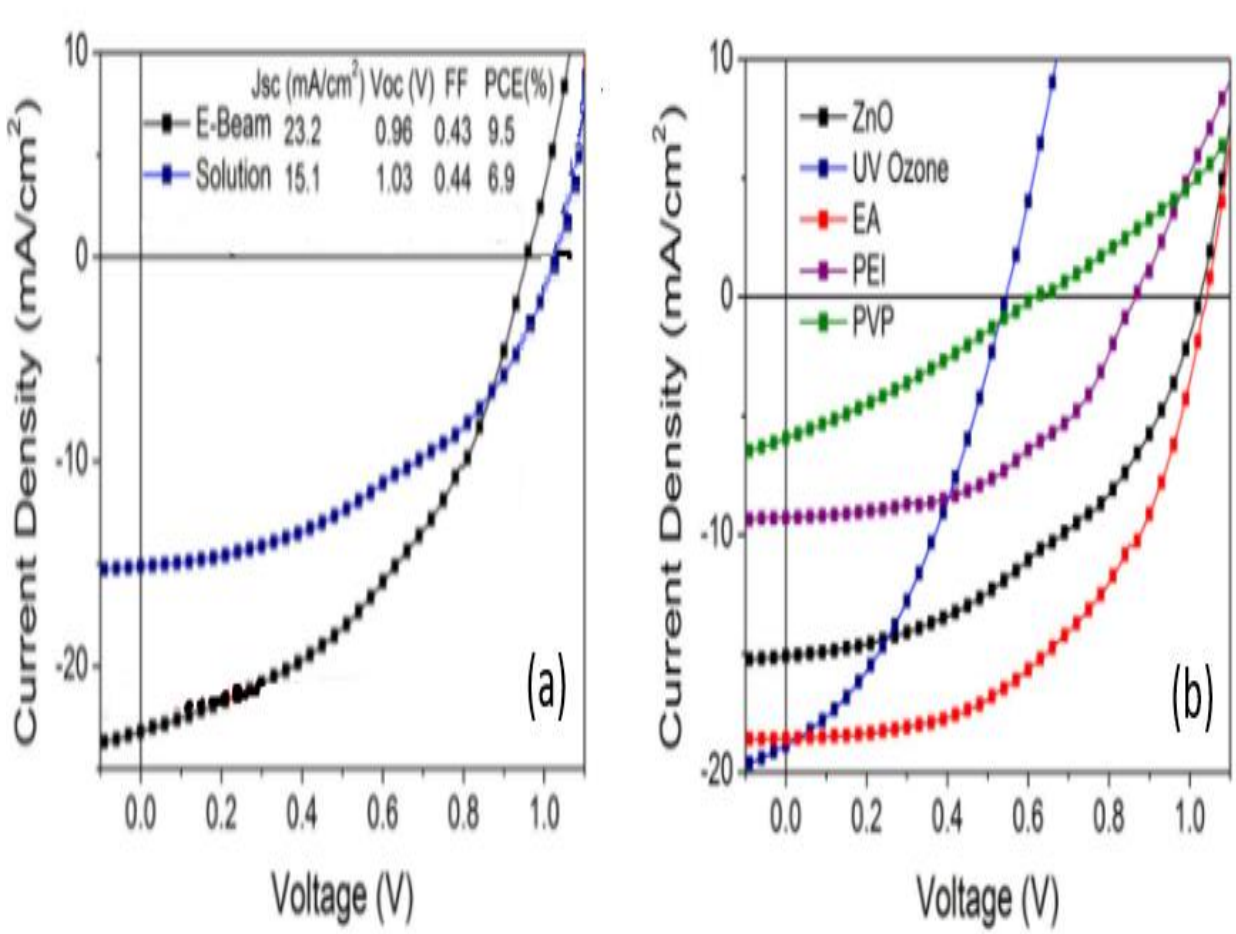

Fig. 4 (a) Current–voltage variations of PSCs with ZnO ETL deposited by e-beam and solution-based techniques. (b) Current–voltage variations of PSCs incorporating ZnO ETLS (solution-processed and treated with UV ozone, ethanolamine, polyethyleneimine, or polyvinyl pyridine). Reproduced with permission [47]

A. Djurišić et al. [47] compared the performance of ZnO based ETLs deposited by e-beam evaporation technique and solution processing [Figure 4(a)]. Researchers examined a variety of surface modification agents including polyethyleneimine, ethanolamine and polyvinyl pyridine. Figure 4 (b) shows the remarkably impact of the surface handling of the ZnO ETL on the performance of perovskite solar cell. The substandard performance along with noticeable diminutions in the fill factor and open-circuit voltage was observed in the case of UV ozone treated ZnO ETL. Surface treatment with polyethyleneimine or polyvinyl pyridine was observed to be unfavorable for the performance of photovoltaics. As discussed in this study, the surface treatments with only ethanolamine led to an enhancement of the PSCs efficiency along with rise in short-circuit current density and fill factor.

Thus, the different deposition techniques and treatments after deposition, remarkably impacts the surface characteristics of ZnO, ZnO/perovskite boundary, superiority of perovskite film and subsequently the efficiency of PSCs.

4.3. Doped ZnO based PSCs

Improvements in PSCs can also be accomplished by doping. Doping is well known and efficient method for improvements of the electronic features of metal oxide semiconductors [48]. ZnO doping generally increases the free charges and therefore increase the conductivity of solar cell devices [49]. The doping of ZnO can be done either by substituting the Zn^{2+} cations or the O^{2-} anions. Replacement of Zn^{2+} by any other cation is probable to change the conduction band while replacement of O^{2-} with any other anion may change the valence band. Hence, the doping ZnO can move the Fermi level towards the conduction band and this helps to upsurge the conductivity. This also help to facilitate the work function.

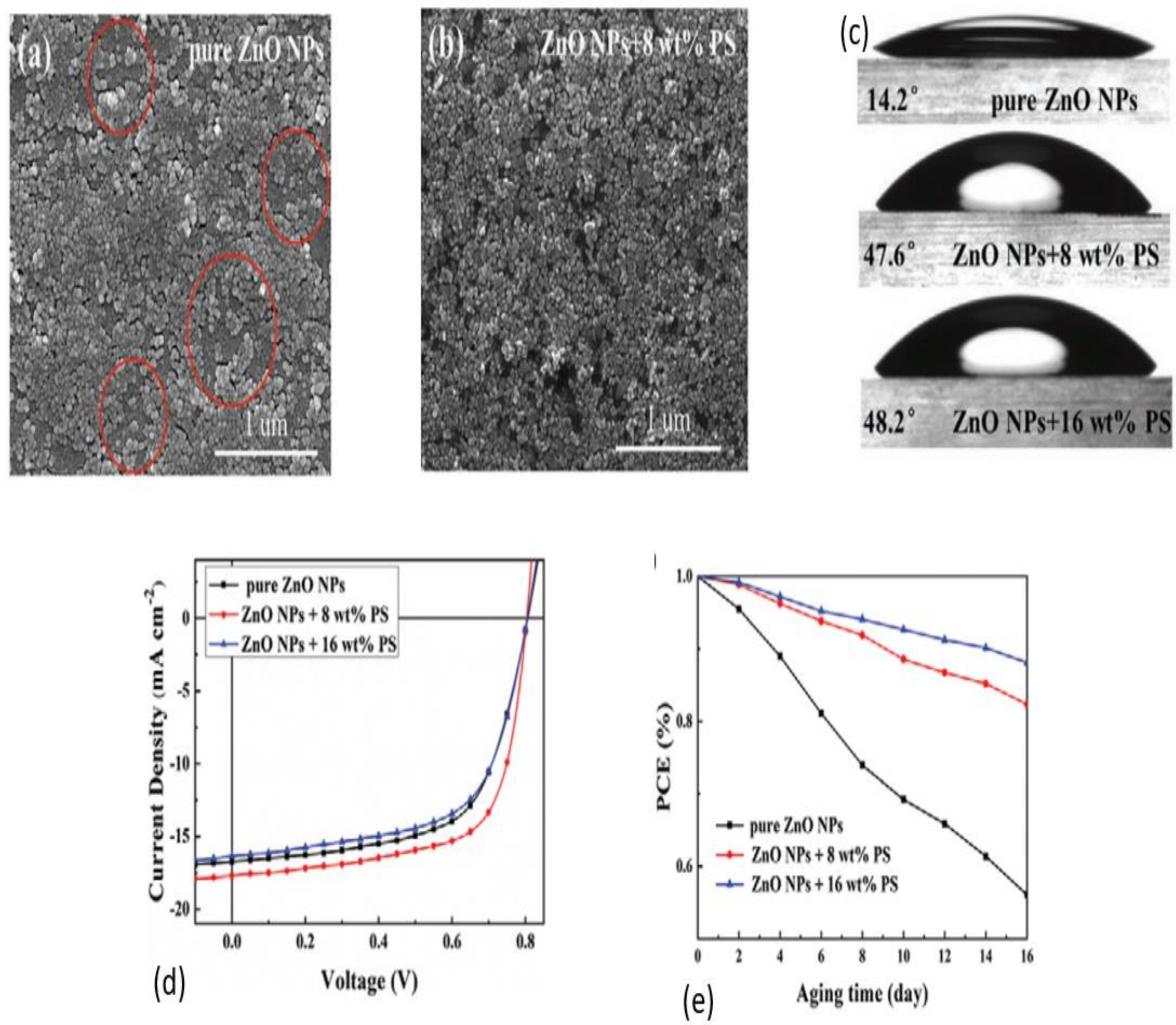

Fig.5 SEM results of (a) pure ZnO nanoparticles film, (b)ZnO nanoparticles film doped with 8 wt.% Polystyrene, (c) measurement of water contact angle for pure ZnO nanoparticle film, 8 wt.% polystyrene doped and 16 wt.% polystyrene doped ZnO nanoparticles film, (d) J–V characteristics and (e) ambient stability of device with different ETLs with different doping concentrations kept in the atmosphere without encapsulation. Reproduced with permission [50]

P.Fan et al. [50] described a simple, efficient and cost-effective technique of adding polystyrene into the ZnO nano particles based ETL to manufacture the better performing PSCs. The doping of polystyrene in optimum amount gives a more uniform ZnO nanoparticle based ETL. This doping produces more ways for electron transport and even mechanical strength of ETL gets better. The surface properties of the ETL [Fig 5 (a) & (b)] also gets modified with doping of polystyrene in ZnO by reducing the hydrophilicity of the surface [Fig. 5(c)]. The doping makes better interaction between the ZnO ETL and the active layer and hence improves exciton dissociation and the carrier collection capacities from the active layer to ETL. Ultimately, the energy conversion efficiencies of perovskite solar devices increase from 8.49% to 9.54% [Fig. 5(d)] with an enhanced short circuit current density and fill factor and the device showed improved stability in environments with high humidity [Fig. 5(e)].

Z. L. Huang et al. used $Al(NO_3)_3{\cdot}9H_2O$ as the source of Al into ZnO nanorods lattice using the hydrothermal process, so that characteristics of ZnO nanorods can be improvise to design PSCs with high performance [51]. They observed Al-doped ZnO nanorods with larger band gap and better electrical conductivity. The steady-state photoluminescence demonstrates effective extraction and collection of charge at Al-doped ZnO nanorods/perovskite layer interface. The optimized PSC have shown short-circuit current density of 21.93 mA/cm^2 , open-circuit voltage of 0.84 V and a fill factor of 57% . The examined device yield a PCE of 10.45% that was 23% greater than the ZnO nano rods without doping. A.Baktash et al. [52] examined the effect of ZnO ETLs doped with magnesium on the performance of perovskite solar device at varying temperatures and observed the improvement in the efficiency of device from 16.78% to 19.57% with increase of doping level up to 10%. C.Bhoomanee et al. [53] observed that doping a small amount of Al with ZnO can improvise the physicochemical properties of ZnO. PSCs based on Al doped ZnO based ETL have shown the highest V_{oc} and J_{sc} with improved and steady performance.

J.H. Kang et al. [54] observed the effect of a new sequence of composite metal oxide on the performance of n-i-p PSCs and concluded the outstanding increment in J_{SC}, V_{OC}, FF and stability of PSC device. The superiority of the perovskite film was also observed to be dependent on the metal oxides used. The tungsten doped indium zinc oxide for ETL, among all the testified metal oxides investigated in their research, was observed to produce optimum results.

5. Challenges faced by ZnO ETLs based PSCs

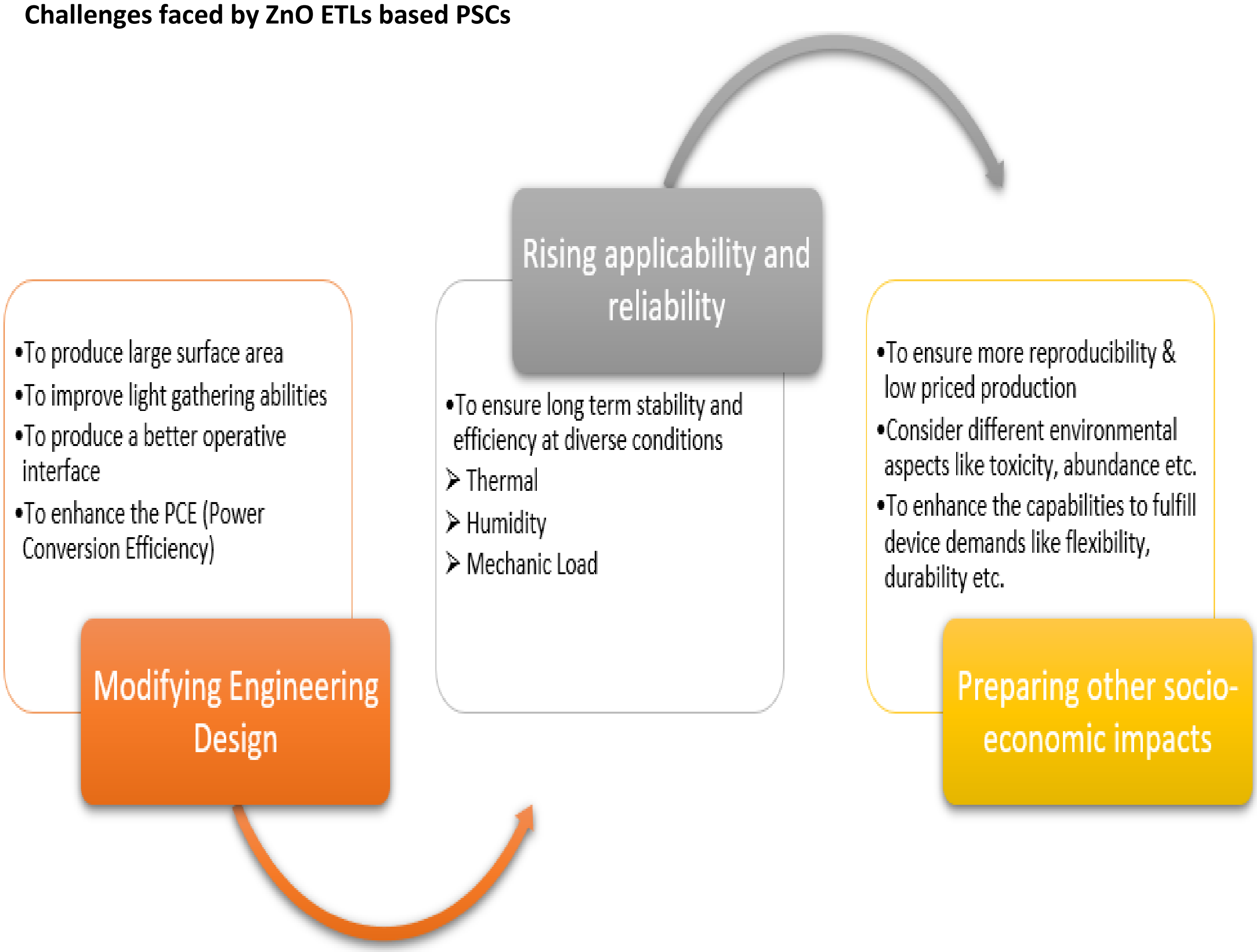

Fig 6 Challenges face by the solar technology with ZnO ETL

In spite of the advancement in PSC that have been attained by using ZnO for the ETLs, there is still a scope of betterment. In the fig. 6 the major issues that are essential to be resolved so as to achieve superiority by ZnO in solar cell technologies. As ZnO ETLs can be easily fabricate at low temperatures, this make it companionable with flexible substrates and thus facilitate the production of perovskite solar cells at large-scale in the future. Although a large no of improvements have been done to use ZnO as ETLs in PSCs, still the problem of device instability is a major issue for their practical applications. These complications are because of chemical instability at the boundary between the ZnO ETL and perovskite absorber layer, which is actually an outcome of protonation reaction between ZnO ETL and organic cations of perovskite absorber layer. This reaction accelerates the decomposition of perovskite material. Numerous strategies have been used to resolve this issue such as synthesis of a ZnO nanocomposite, introducing a barrier layer between ZnO ETL and the perovskite absorber layer, doping into ZnO or passivation of the ZnO film .Interface engineering in PSCs has been an effective way to achieve the better performance and high stability of the device [55-64]. With all these changes, higher energy conversion efficiency and longer life span of PSCs in surroundings with diverse thermal conditions, humidity and mechanical loading would be possible.

6. Future Aspects

The evolving solar cell generations have not achieved the saturation into the market. Therefore, development in accomplishing a low-priced processing of ZnO ETLs with good reproducibility using a green technology, which would offer livability and environmental-friendliness. This would enhance the positive effects on the socio-economic aspects. In addition flexibility, durability of the device are also a demand of the market.

Conclusion

In the past few decades, the PSCs has shown epic performance. Several novel perovskite compounds and different fabrication techniques have been industrialized to design a well performing PSC. ZnO can be a powerful alternative to the extensively used TiO_2 for the ETLs. In addition to this, ZnO nanomaterials can be easily fabricate with less energy consumption and in low budget. In this article, the performance of PSCs using unlike nanostructures of ZnO, different deposition techniques, post deposition treatments and using doped ZnO have been reviewed. To improvise of ZnO ETLs so as to decrease the recombination and to enhance the charge collection capabilities are topmost demand of the time. The stability of device using ZnO based ETLs, is another significant issue and must be resolved in future. However PSCs with ZnO based ETLs, have accomplished an outstanding performance and it is continued to the march towards the photovoltaic technology with highly efficiency and low-price.

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