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Recent Advances of ZnO-Based Perovskite Solar Cell

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Abstract

Perovskite solar cells (PSCs) have developed rapidly over the past few years, and the power conversion efficiency (PCE) of PSCs has exceeded 25%. It has the characteristics of low cost, high efficiency, simple process and so on, and hence has a good development prospect. Due to the difference in electrons and holes diffusion lengths, electron transporting materials (ETMs) play a crucial role in the performance of PSCs. ZnO electron transport layer (ETL) has the advantages of high electron mobility, high transmittance, suitable energy level matching with neighbor layer in PSCs, low temperature preparation and environmental friendliness, so it has become the main application material of electron transport layer in perovskite solar cells. In this review, the application of ZnO-ETMs in PSCs in recent years is reviewed, and the effect of ZnO-ETMs on the performance of PSCs is also introduced. Finally, the limitations of ZnO-ETMs based PSCs and the methods to solve these problems are discussed, and the development prospect of PSCs is prospected.

Keywords: Perovskite solar cells; ZnO; ETM; Power conversion efficiency; Stability.

1. Introduction

1.1. Perovskite solar cells

The solar energy is inexhaustible and is one of the most environmentally friendly energy sources. 0.1% of the total energy radiated from the sun to the earth is enough to meet the consumption of the whole human society[1] . Solar cells can be divided into the following generations according to the materials: (1)Silicon based solar cells mainly refer to solar cells based on the composite of monocrystalline silicon, polycrystalline silicon and amorphous silicon. The first piece of silicon solar cells in 1954 Bell LABS was born in the United States, the PCE is only 6%[2], after several years of development, at present the highest PCE can reach 26.7%[3].This kind of solar cells has high stability and high photoelectric conversion efficiency, but it requires a lot of materials and high cost. The highest efficiency that can be achieved in the laboratory is 27.6% at present, as shown in Figure 1.However, its efficiency is very close to the Shockley-Kuisser limit (≈30%)[4], and its room for rise is limited. (2)Thin-film solar cells, mainly cadmium selenide CdSe[5], cadmium telluride CdTe[6], copper indium tin CuInSe2[7], copper Indium gallium Selenium CIGS[6], copper zinc tin sulfur CZTS[8] solar cells, etc.

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The photoelectric conversion efficiency of this kind of battery is relatively high, the light absorption layer is relatively thin, which can reduce the material consumption, and the price is cheap. It occupies about 10% of the global market share. However, some of these materials are toxic or the material reserves are small, so they are not suitable for large-scale production and use. (3)The new solar cells mainly include dye-sensitized solar cells, perovskite solar cells, quantum dot solar cells, and stacked solar cells.

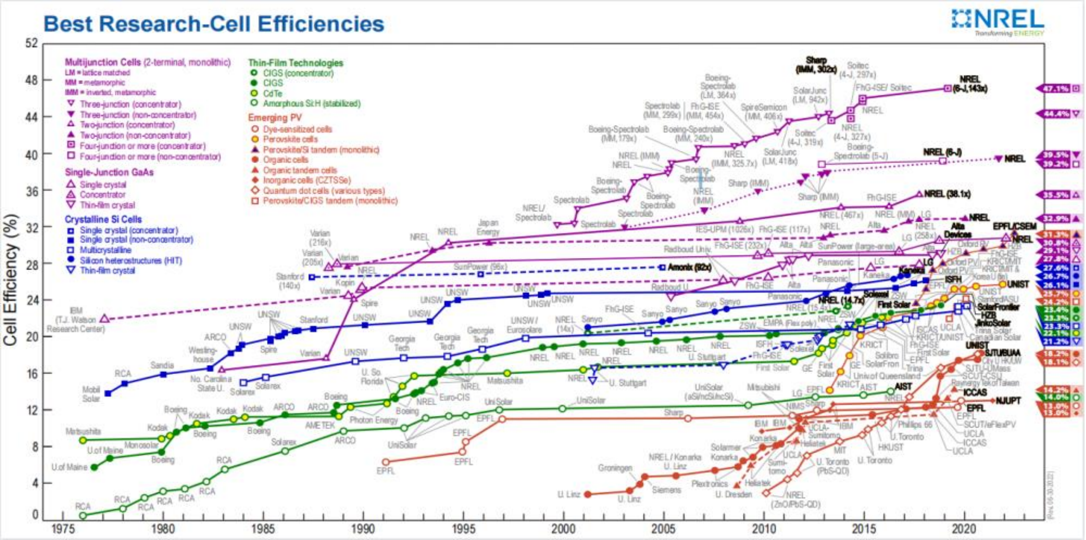


Figure 1: The latest solar cell efficiency diagram certified by NREL.

Perovskite solar cells have attracted the most attention in the field of solar cells in recent years. In view of the excellent photoelectric performance of organic-inorganic hybrid perovskite materials, the PCE of this kind of cells has exceeded 25% in just a few years[9,[10], as shown in Figure 1. Organic-inorganic hybrid perovskite is a promising material for solar cells with high efficiency and low cost. ABX3 is the chemical formula of perovskite materials, where A is usually cation or cationic group with large size, B is usually cation of moderate size, and X is an anion. The crystal structure of perovskite material is shown in Figure 2: In the crystal structure of perovskite, atom A occupies the eight vertices of the hexahedron, atom X occupies the six face center positions, and atom B occupies the body center position[12, 13 , 14, 15]. In the organic inorganic hybrid perovskite materials, A general for cesium ion (Cs+), methylammonium cations(MA+) , formamidinium cations (FA+). B ions are usually Pb2+ and Sn2+.X is an anion, usually oxygen ion (O2-) and halogen element ions, such as chloride ion (Cl-), bromide ion (Br-) and iodide ion (I-) [16,17,18,19]. Organic-inorganic hybrid perovskite materials have unique optoelectronic properties compared with common pure organic or pure inorganic semiconductor materials[11,20,21]. First, the hybrid perovskite material has a large Bohr radius and dielectric constant, and also has a small exciton binding energy. These characteristics enable the photogenerated excitons in the perovskite material to rapidly separate into free carriers at room temperature[14,15,22,23]. Second, hybrid perovskite materials have longer carrier diffusion distance and higher carrier diffusion velocity[24,25,26,27]. Third, the most common hybrid perovskite material has a forbidden band width of about 1.5 eV, which makes the hybrid perovskite material have high light absorption capacity in the visible light band[14]. The above characteristics make organic-inorganic hybrid perovskite materials have great application potential in the field of photovoltaics[11,28].

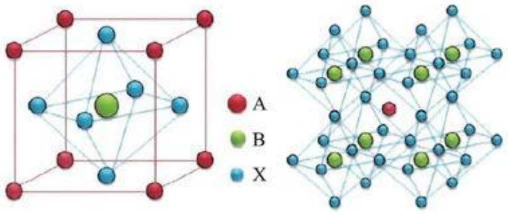


Figure 2: The crystal structure of perovskite, in the crystal structure of organic–inorganic hybrid perovskite, A = cation or organic cation group, B = Pb^{2+} or Sn^{2+}, and X = halogen ion.

Perovskite solar cells usually adopt porous structure and planar structure, including positive NIP structure and anti-PIN structure respectively. Figure 3 shows a schematic diagram of several common perovskite solar cell structures. They are usually composed of electron transport materials, perovskite light absorption materials, hole transport materials and electrodes. When perovskite solar cells are exposed to sunlight, perovskite materials absorb incident photon energy to produce excitons. At the cell interface (at the perovskite material/carrier transport layer interface) and in the perovskite film, excitons are separated into electrons and holes that are extracted by the respective transport material and transferred to the electrode. By applying a load to a solar cell to form a complete loop, an electric current can be generated in the circuit. The role of the electron transport material in the structure is to balance the difference between the hole and electron diffusion distance. At the same time, the electron transfer material also acts as a hole barrier material to prevent the recombination of electrons and holes at the interface. The selection of electron transfer materials has an important impact on the performance of perovskite solar cells.

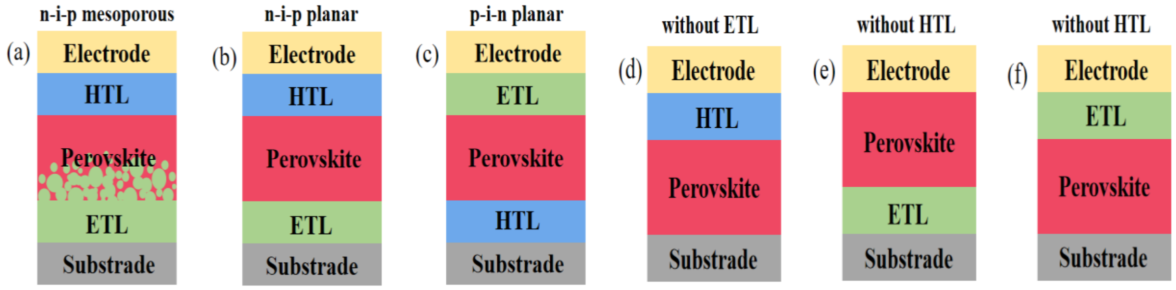


Figure 3: Schematic representation of a common structure of a perovskite solar cell.(a)n-i-p type mesoporous structure.(b)n-i-p planar structure.(c)p-i-n planar structure.(d)without ETL structure.(e)(f)without HTL structure.

1.2. The requirements for the electronic transport layer

Typically, in conventional perovskite cell structures, a dense electron transfer layer is inserted between a transparent conducting oxide layer (such as FTO) and a mesoporous scaffold. The dense layer can facilitate electron transport from the mesoporous scaffold to the FTO layer, thereby reducing charge recombination. The dense layer has a greater impact on the performance of PSCs and thus has been extensively studied[29,30,31,32]. To meet the performance requirements of solar cells, electron transport materials must meet the following conditions:(1) It has good transmittance in the visible light band; (2) The energy level position of electron transport material must match the energy level position of perovskite material; (3) Higher carrier mobility; (4) Low cost and easy fabrication[14,15,22,23]. Among various dense layers, TiO2 is currently the most widely used. Its energy level positions match those of commonly used perovskite materials, and the valence band top position is deep, which can effectively block hole transport and suppress carrier recombination. TiO2 is still the preferred electron transfer material for preparing high-performance perovskite solar cells due to its suitable band gap, high transparency and excellent performance. The preparation methods of TiO2 dense layers include spin coating, electrochemical deposition, thermal oxidation, atomic layer deposition or spray pyrolysis[23,33,34,35]. Kim and colleagues[37] synthesized TiO2 dense layers by spin-coating titanium bisisopropoxide solution (0.1 M) on FTO substrates. Weijun Ke and colleagues[38] deposited TiO2 on FTO substrates by thermal oxidation. Snaith's research group[39] combined vacuum dual-source thermal deposition technology with MAPbI3-xClx and TiO2 dense layers, and the constructed n-i-p-type FTO/TiO2/MAPbI3-xClx/Spiro-OMeTAD /Ag structure perovskite solar cell achieved a photoelectric conversion efficiency of 15.4%. Professor Park’s group[40] achieved an efficiency of 17.01% for a TiO2 superstructure device constructed by a two-step spin coating method. Professor Seok and his collaborators[42] used FAI to replace MAI, and adopted solvent engineering to prepare FAPbI3 thin films by the direct intramolecular exchange method between PbI2 and FAI using DMSO. The PCE of perovskite solar cells constructed (FTO)/bl-TiO2 /mp-TiO2/FAPbI3/PTAA/Au structure exceeds 20%. Figure 4a is a cross-sectional view of the device, from which it can be seen that the interfaces between the layers are in close contact. Figure 4b shows the SEM images of the surface of FAPbI3 thin films prepared by intramolecular exchange process (top) and conventional method (bottom). It can be seen from the figure that the crystal size of FAPbI3 prepared by the intramolecular exchange process is larger and the film coverage is higher. The J-V curve in Figure 4c shows that the perovskite solar cell can effectively avoid hysteresis, and the quantum efficiency of the device can reach 90% from the IPCE spectrum[42]. Based on TiO2 electron transport layer and Spiro-OMeTAD hole transport layer, Professor Gratzel's research group dissolved FAI, PbI2, MABr and PbBr2 together in the mixed solution of DMSO and DMF. By optimizing the ratio of FAI and PbI2, finally, the hysteresis effect is effectively avoided, 20.8% conversion efficiency was obtained[43].

In the actual process, the preparation of dense or porous TiO2 films usually uses spray pyrolysis and spin coating. In the process of preparing TiO2 using these methods, high temperature calcination (generally 500℃) is usually required to transform TiO2 from an amorphous state to a anatase phase to enhance the carrier transport capacity of the film. Although the high-temperature calcination process is beneficial to improve the battery performance, it also limits the application range of TiO2 materials and increases the battery manufacturing cost to a certain extent. The electron mobility of organic-inorganic hybrid perovskite materials is roughly 7.5 cm2V-1s-1, while the electron mobility of TiO2 materials is roughly in the range of 0.1-4 cm2V-1s-1, the lower electron mobility will directly lead to the degradation of solar cell performance[13]. Besides TiO2 materials, fullerenes and their derivatives are also widely used as electron transport materials[44,45,46,47].

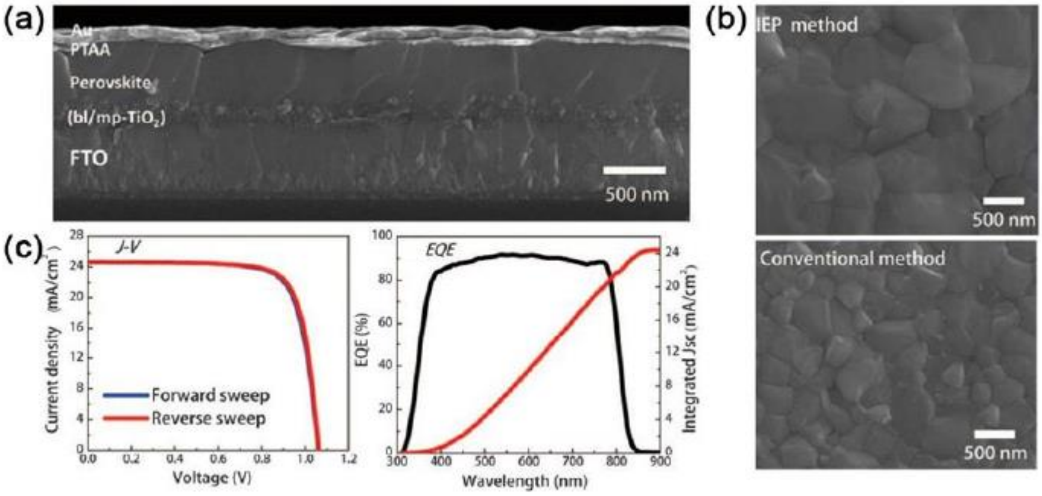
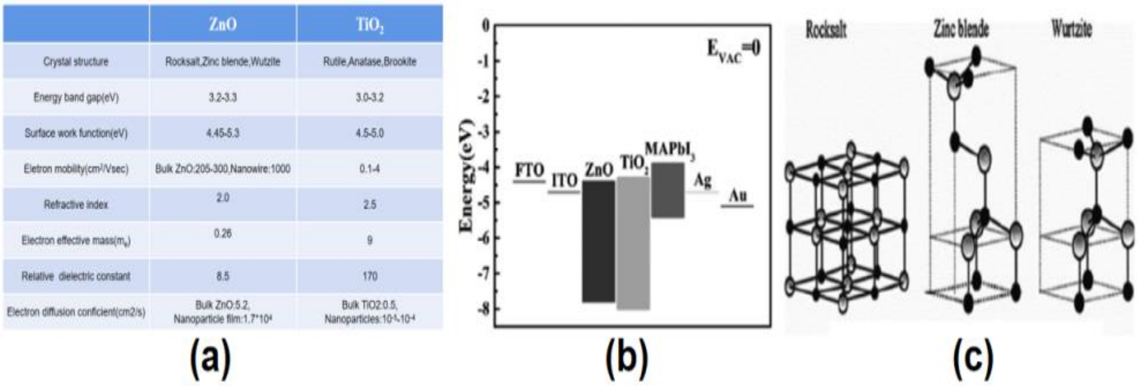


Figure 4: SEM, J-V and EQE tests of the device: (a) Cross-sectional SEM image of the device consisting of FTO/bl-TiO2/mp-TiO2/FAPbI3/PTAA/Au; (b) SEM images of FAPbI3 films obtained by intramolecular exchange process and conventional method; (c) J-V curves and EQE spectrum of the device based on FAPbI3 fabricated by intramolecular exchange process [42].

1.3. The advantages of ZnO ETL

ZnO is also a commonly used electron transport material. Before being used in perovskite solar cells, as an alternative to TiO2, the performance of ZnO electron transport materials has long been demonstrated in the fields of dye-sensitized cells and polymer cells. ZnO has good visible light transmittance, high electron mobility, suitable work function and dissolution process, and is a promising electron transport material in perovskite solar cells[48,49,50,51]. Therefore, perovskite solar cells based on ZnO electron transport layers have also been systematically studied, and perovskite solar cells based on ZnO electron transport materials have also achieved high photoelectric conversion efficiency[52].Although there is still a certain gap with the highest efficiency of perovskite solar cells based on TiO2 materials, ZnO is still an ideal alternative material for TiO2. ZnO is an important IIB-VIA direct band gap semiconductor material. As shown in Figure 5, ZnO has similar physical properties to TiO2. Its conduction band bottom is at -4.2eV, and its forbidden band width is 3.37eV, which is similar to that of TiO2. The energy band position is very close to the forbidden band width, which matches the energy level position of materials such as MAPbI3 and FAPbI3, which can effectively improve carrier extraction and transport efficiency. ZnO has similar band positions and physical properties to TiO2, but has higher electron mobility, which can potentially improve electron transport efficiency and reduce recombination losses as an ETM[11]. The exciton binding energy of ZnO material at room temperature is 60 meV, which makes it have great application potential in short-wavelength optoelectronic devices. Compared with TiO2 materials, ZnO materials have two obvious advantages: ZnO materials have higher electron mobility, which is very beneficial for improving the carrier transport efficiency of solar cells and suppressing carrier recombination. Some methods of preparing ZnO materials do not require high temperature treatment[11,53,54,55]. These properties make ZnO an excellent ETM for PSCs. Therefore, research on ZnO-based solar cells can help improve the performance of PSCs.

This paper briefly summarizes the properties of ZnO materials and systematically reviews the application of ZnO-ETM in PSCs. An overview of the development of ZnO-based PSCs is presented. The important effects of the preparation and optimization of ZnO-ETM on the performance of solar cells are described. In addition, the limitations of ZnO-ETM are discussed and some suggestions for further optimization and design of ZnO-ETM-based PSCs are provided.



	ZnO	TiO_2
Crystal structure	Rocksalt,Zinc blende,Wutzite	Rutile,Anatase,Brookite
Energy band gap(eV)	3.2-3.3	3.0-3.2
Surface work function(eV)	4.45-5.3	4.5-5.0
Eletron mobility(cm^2/Vsec)	Bulk ZnO:205-300,Nanowire:1000	0.1-4
Refractive index	2.0	2.5
Electron effective mass(m_e)	0.26	9
Relative dielectric constant	8.5	170
Electron diffusion conficient(cm2/s)	Bulk ZnO:5.2, Nanoparticle film:1.7*10^{4}	Bulk TiO2:0.5, Nanoparticles:10^{-5}-10^{-4}

Figure 5: a) Comparison of the electrical properties of ZnO and TiO2.[53][54][56] b) The energy level of ZnO, TiO2, and other usually used materials in PSCs.[53] c) Three different crystal structures of ZnO. [57].

2. The common preparation methods of ZnO ETL

2.1. PSCs based on ZnO thin films

There are many preparation methods of ZnO thin films, and different preparation methods have a great influence on the formation of ZnO thin films, so it is very important to choose a suitable method to prepare ZnO thin films. Common preparation methods include: sol-gel method, magnetron sputtering method, atomic layer deposition method, electrostatic spraying method, etc.

2.1.1. Sol-gel method

The sol-gel method has become the most commonly used method for the preparation of ZnO electron transport layers due to its low energy consumption and large-scale production requirements. D. Liu and colleagues[58] used the sol-gel method to prepare the ZnO electron transport layer for the first time, and on this basis prepared a planar structure perovskite solar cell, the photoelectric conversion efficiency of the cell reached 15.7%. As the thickness of the ZnO film increased from 0 to 25 mm, the PCE of PSCs increased from 2.4% to 14.4%. When the thickness of the ZnO film continued to increase to 70 nm, the PCE decreased to 12.9%. Park research group[59] prepared ZnO electron transport layer by sol-gel method, and after high temperature calcination at 450℃, the PCE of the device can also reach 11%.

2.1.2. Magnetron sputtering method

Magnetron sputtering method[65,66] can prepare high-quality ZnO thin films by controlling the power, time, and sintering temperature of magnetron sputtering equipment. The radio frequency sputtering method in magnetron sputtering is often used to prepare dense ZnO thin films. The ZnO thin films prepared by radio frequency sputtering method have the advantages of low defect, high density and uniform distribution. Radio frequency sputtering is a vacuum coating technique. During its working process, argon gas is blown into a vacuum chamber, and a high-energy particle flow is formed under the action of a high-frequency high-voltage electric field. High-energy particle flow bombards the target, sputtering out atoms and molecules on the surface of the target material, and these particles deposit on the substrate to form a uniform and dense film.Factors that affect the performance of the film include the composition and purity of the target material, the pressure of the working gas, the ratio of different working gases, the radio frequency power, etc.

By optimizing these parameters, high-quality ZnO films with high transmittance and good optoelectronic properties can be obtained. The research group of Tseng[60] studied the effect of radio frequency parameters on ZnO thin films. The ZnO thin films were prepared by radio frequency sputtering with different O2/(Ar+O2) ratios. The resulting device structure was (ITO)/ZnO/MAPbI3/Spiro-OMeTAD/Ag. The device formed by the ZnO thin film prepared under the condition of pure Ar has the best performance, with a PCE of 15.9%.

The PCE of the ZnO thin film prepared under the condition of O2/Ar mixture is about 12%. Zhao's research group[61] compared the ZnO films formed by RF sputtering and the sol-gel method, and found that the thermal stability of ZnO films formed by RF sputtering was higher than that of ZnO formed by sol-gel method film. Their reported device structure is AZO/MAPbI3/Spiro-OMeTAD/Au. the highest PCE reached 12.6%. Wu's research group[56] formed Al-doped ZnO thin films (AZO) by radio frequency sputtering, and explored the device properties of AZO thin films and ZnO thin films. The thermal stability of the perovskite layer deposited by the ZnO film prepared by the radio frequency sputtering method is also higher than that of the ZnO film prepared by the sol-gel method, and the highest efficiency of the device is 17.6%.

2.1.3. Atomic layer deposition

Atomic layer deposition (ALD) is a chemical vapor deposition technology, which has the advantages of simple process, high surface coverage, and good transport ability of the prepared electron transport layer. Therefore, ALD is widely used in the preparation of ultra-thin, dense and high-quality ZnO film. Lee 's research group[62] prepared ZnO thin film with a thickness of 5-40nm through ALD. The device structure is ITO/ZnO/MAPbI3/Spiro-Ometad /MoO3/Ag. When the thickness of the ZnO film is 30 nm, the performance of the device is the best, and the PCE reaches 7%. Ding's research group[63] prepared ZnO thin films by ALD method. By comparison, it is found that the thermal stability of the perovskite layer deposited on the ZnO films prepared by ALD method is higher than that of the ZnO films prepared by solution method.

In addition, it is found that when the preparation temperature is 70℃, the performance of the formed thin-film device is the best, the device has the highest efficiency reached 13.1%. Zhang's research group[64] prepared ZnO thin film by ALD method, and prepared a layer of Al2O3 thin film by ALD method on ZnO thin film. The ZnO film prepared by the ALD method has a better densification effect. When the thickness of the Al2O3 film is At 4 Å, the device performs the best with an efficiency of 15.55%.

2.2. Mesoporous PSCs based on ZnO nanomaterials

In order to make the ZnO ETL have better photoelectric properties, some people propose to change the structure of ZnO to achieve this effect, and people have prepared many different ZnO nanostructures as the ETL.[67,68] Because of its easy crystallization and anisotropic growth properties, ZnO materials can be fabricated into a variety of nanomaterials with unique optoelectronic properties, such as nanoribbons[69,70,71], nanotubes[72,73], nanorings[74,75,76], nanoflowers[77,78,79], nanowires[80,81,82], nanorods[83,84], nanosheets[54] etc. (as shown in Figure 6) can be prepared by a relatively simple method.[84] On the one hand, ZnO nanomaterials can provide a larger specific surface area, increase the contact area between the electron transport material and the perovskite film, and improve the carrier transport and extraction efficiency. On the other hand, due to the small size effect of nanomaterials, nanomaterials will exhibit some special properties in electron transport or light transport, such as surface effect, quantum confinement effect or photon localization effect, etc. Especially for one-dimensional(1D) ZnO nanocolumns, the C-axis direction has high carrier mobility[53]. ZnO nanomaterials, such as nanoparticles, nanowires and nanopillars, have been widely used in many fields such as dye-sensitized cells and organic solar cells. There are also many methods for preparing ZnO nanomaterials, such as sol-gel method[85], water bath method[86][87][88], combustion synthesis method[89], etc. In 2013, Hagfeldt and colleagues[90] used ZnO in perovskite solar cells for the first time and obtained a photoelectric conversion efficiency of 5%. In the same year, Kumar and colleagues[91] used chemically deposited ZnO nanorods (NRs) as the electron transport layer and increased the efficiency to 8.9%. Meanwhile, devices based on polyethylene terephthalate (PET) flexible substrates achieved an efficiency of 2.62%. Hereafter, Park and colleagues. also chose ZnO NRs as the electron transport layer, which provided a more direct transport channel for electron transport, increasing the efficiency to 11.13% and 14.35%[59,92]. Pauporté and colleagues found that compared with ZnO nanoparticles, ZnO nanowires prepared at low temperature can shorten the diffusion path of carriers, thereby improving the efficiency of perovskite solar cells [93,94,95]. In 2015, Amassian and his collaborators used N-doped ZnO NRs (N:ZnO NRs) as the electron transport layer material, and achieved a photoelectric conversion efficiency of 16.1% under the premise of effectively avoiding the hysteresis effect, which was also the highest value of ZNO-based perovskite solar cells at that time.

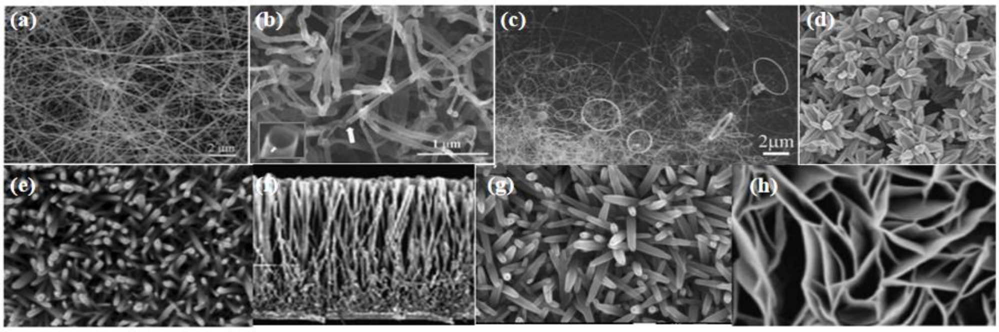


Figure 6: The SEM images of several ZnO nanomaterials with different structures:(a)nanoribbons[70], (b)nanotubes[72],(c)nanorings[75],(d)nanoflowers[78],(e)nanowires[80],(f)cross-sectional views of nanowires[103],(g)nanorods[92],(h)nanosheets[54].

3. The PV devices based on ZnO ETL

3.1. Traditional devices

Organic-inorganic hybrid perovskite solar cells are currently the most studied perovskite solar cells, and organic-inorganic hybrid perovskite materials are one of the most promising materials for the preparation of high-efficiency and low-cost solar cells. The most commonly used A ion for this material is CH3NH3+(MA) and NH=CHNH3+(FA). B ions are inorganic cations such as Pb2+and Sn2+. X represents a halide ion, such as Cl-, Br- and I-. As a widely used ETM, ZnO is an alternative material for TiO2 in DSSCs and polymer solar cells due to its similar energy band position and physical properties to TiO2[11]. Liu and Kelly's group synthesized ZnO nanoparticle thin films by solution method and applied them to planar heterojunction PSCs. Its structure is ITO/ZnO/MAPbI3/Spiro-OMeTAD/Ag. The ZnO nanoparticle films with the thickness of 0-70nm were obtained by spin coating. The PCE of PSCs based on 25nm ZnO thin films as high as 15.7% was obtained. Under the action of thermal stress, the organic cations in the perovskite material will undergo a protonation reaction with ZnO, which in turn triggers the decomposition of the perovskite layer from the interface. As a result, ZnO is more used in pure inorganic perovskite solar cells, and the A-site cation of such perovskite solar cells is usually Cs+.

In recent years, ZnO-based PSCs have also been studied systematically. The optimal PCE of ZnO-based PSCs is about 17%. A small amount of Al3+ can replace the Zn2+ of the lattice point, as a dopant to improve the conductivity of the semiconductor ZnO. Chun-guey Wu's research group[56] prepared high-quality, fully covered Al doped ZnO (AZO) thin (~20 nm) films on ITO substrates by sputtering. The dense and uniform MAPbI3 absorbent can be deposited on ETL by two-step spin coating method. The best AZO based perovskite cell achieves the highest PCE of 17.6% with the Voc of 1.07 V, both of which are the highest values we know so far for ZnO-based PSCs.

3.2. Flexible devices

In recent years, cryo-electron transport materials, such as ZnO[89] and SnO2 [98] has been widely studied for its low cost and compatibility with flexible PSC[99,100,101]. In addition, the electron mobility rate of perovskite materials is about 7.5 cm2V-1s-1, while the electron migration rate of TiO2 is only 0.1-4 cm2V-1s-1. The low electron mobility of TiO2 leads to hindered electron transport, which affects the performance of perovskite solar cells[13]. Compared with TiO2, ZnO not only has a higher electron transport rate (205-300 cm2V-1s-1), but also can effectively avoid the high temperature annealing process[55,102]. ZnO materials with excellent crystallinity can be obtained through various low-temperature solution processes, they are more suitable for the preparation of flexible perovskite solar cells[103]. In 2014, Kelly's research group reported the preparation of ZnO nanoparticles as an electron transport layer by a solution method, which reduced the preparation temperature of the device to below 65℃, and at the same time increased the cell efficiency to 15.7%. In addition, a perovskite solar cell with a device area of 1 cm2 was assembled on an ITO/PET flexible substrate with a photoelectric conversion efficiency of 10.2%.[58] The efficiency of ZnO-based perovskite solar cells (15.96%) is higher than that of TiO2-based perovskite solar cells (15.20%), and the hysteresis effect is weaker. The characterization results show that, however, based on the low temperature advantage of preparing the ZnO electron transport layer, a flexible solar cell with a polyethylene naphthalate (PEN)/ITO/ZnO/CH3NH3PbI3/PTAA/Au structure was realized on a PEN flexible substrate. Figure 7a shows the EQE spectrum of the flexible solar cell and the transmission spectrum of the PEN/ITO film. Figure 7b shows the J-V curve of the flexible perovskite solar cell, whose maximum efficiency can reach 15.6%. The efficiency of the flexible device did not change significantly after different degrees of bending, indicating that the device has good mechanical stability[104]. Tian's group[105] prepared ZnO electron transport layer by sol-gel method at low temperature of 150℃, and studied the effect of ZnO layer thickness on device performance. The thickness of the ZnO layer varies between 0-60 nm. The performance of the device is optimal at 20nm, with the highest PCE of 13.4%. Ma’s group[106] used carbon as the electrode to fabricate hole-free, metal-free perovskite solar cells on rigid and flexible substrates at low temperature at 120℃. The structure of the device is FTO, ITO/ZnO/CH3NH3PbI3/C electrodes, and the highest PCE of the device on rigid substrate and flexible substrate is 8.73% and 4.29%, respectively. Tian's group[65] used the magnetron sputtering method to prepare PSCs with ZnO thin film as the electron transport layer on flexible substrates, and the prepared device had a high Jsc value (22.4mA/cm2), the highest efficiency of the device reaches 13.4%.

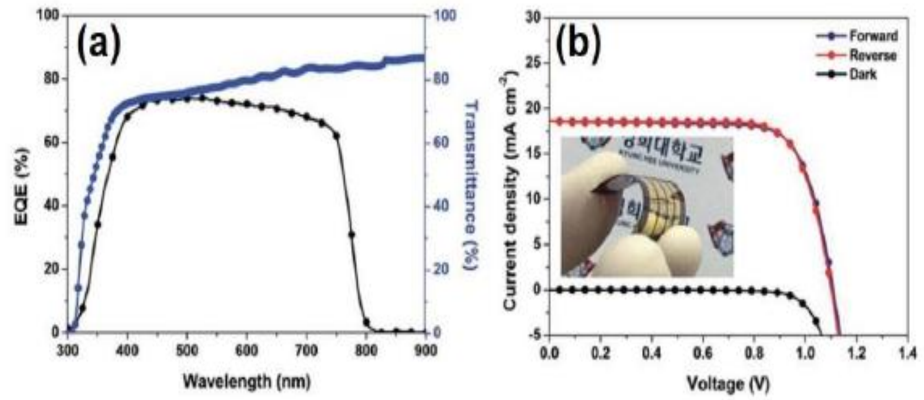


Figure 7: Performance measurements of the flexible ZnO-based perovskite solar cell: (a) EQE spectrum of PEN/ITO/ZnO/MAPbI3/PTAA/Au flexible solar cells and the transmission spectrum of the PEN/ITO film; (b) J-V curves of the flexible solar cells; Inset shows photograph of the corresponding blxible solar cells[104].

4. The challenges and solutions of ZnO ETL

Although ZnO as an electron transport layer is beneficial for electron transport and suitable for the preparation of flexible perovskite solar cells, the performance of ZnO-based perovskite solar cells still needs to be improved, because there are still many problems to be solved.

4.1. Severe interface recombination and solutions

The severe recombination of the surface restricts the further development of ZnO-based solar cells. Similar to other semiconductor materials, point defects affect the electrical and optical properties of ZnO. There are six kinds of point defects in ZnO, namely zinc vacancy (VZn), oxygen vacancy (VO), zinc interstitial (Zni), oxygen interstitial (Oi), zinc inverse crystal (ZnO) and oxygen inverse crystal (OZn)[57]. According to the theoretical calculations and experimental results of Oba and colleagues and Kohan and colleagues among N-type ZnO, the formation energy of VO is the lowest which is 0.02ev, and the concentration is the largest. Zni also has relatively low formation energy and relatively high concentration. The concentrations of these acceptor defects are low due to the high formation energies of VZn, Oi and OZn. Therefore, VO and Zni play key roles in ZnO[107,108]. In addition to these point defects, a large lattice mismatch can be observed at the ZnO/perovskite interface when perovskite material is deposited on the ZnO surface, which has been confirmed by computational analysis[109]. The surface state of ZnO thin films is another source of recombination, and 30% of the atomic bonds in ZnO nanoparticles are dangling bonds[110]. Additionally, once exposed to air, oxygen and water in the air are absorbed by the ZnO surface, which also forms recombination centers. In addition, due to the charge transfer between the adsorbate and the ZnO surface, the adsorbate forms a Schottky barrier-like structure with the ZnO surface, thereby changing the carrier concentration in the surface space charge region. Some adsorbates such as OH molecules can cause band bending and charge accumulation on the surface of ZnO, thereby changing the electrical conductivity of the ZnO surface[111,112].

The high defect density of ZnO-ETL is another important reason why the performance of ZnO-based perovskite solar cells is still lower than that of TiO2-based perovskite solar cells. High-performance ZnO-based perovskite solar cells rely on dense ZnO films with low defects and few pinholes. In order to obtain high-quality ZnO thin films, radio frequency sputtering, electrostatic spraying and atomic layer deposition techniques have been developed. Among them, the electrostatic spraying technique has higher deposition rate and repeatability, but more pinholes in the obtained ZnO films than the other two methods[11]. In terms of eliminating the hysteresis effect, nano-ZnO has received great attention due to its unique advantages such as high specific surface area and effective separation of interfacial carriers[58]. However, it is still extremely challenging to fabricate low-defect, pinhole-less, and tightly-arranged electron transport layers using nano-ZnO particles.

In addition, new defects will also be introduced in the preparation process and the solution process. ZnO materials prepared by chemical methods such as hydrothermal method, chemical bath deposition method, and sol-gel method are unlikely to be pure crystals, and organic species and chemicals in the precursor solutions used in the preparation process will remain or adsorb in the ZnO surface[113,114].

To improve the performance of ZnO-based PSCs, the problem of high recombination loss must be addressed. According to the Shockley-Read-Hall (SRH) theory, there are two technical means to reduce surface recombination: (1) Reduce the density of surface states. (2) Reduce the concentration of surface free electrons and holes. Deposition or growth of a suitable low surface recombination velocity material on the surface can reduce the surface state concentration, and doping can reduce the free carrier concentration, which are the two most commonly used methods[115]. J.Cao and colleagues [52] used MgO to passivate the ZnO surface, while the surface was further modified with ethanolamine. The photoelectric conversion efficiency of the cell is as high as 21.1%. Son and colleagues[92] reported a solution method for preparing TiO2 thin layer on the surface of ZnO nanorods. The surface morphology of TiO2 modified ZnO nanorods is shown in Figure 8a. It can be seen that the surface of ZnO is uniformly covered by TiO2. Figure 8b shows the J-V curves of ZnO nanorods PSCs before and after TiO2 modification. As expected, the photovoltaic performance, especially Voc and FF, were improved to varying degrees, indicating that surface modification is an effective method to inhibit surface recombination. Dong and colleagues [116] and Chen and colleagues[117] also reported similar results. In 2016, Zhang's group modified ZnO nanorods by ultrathin Al2O3 films prepared by ALD method[118,119]. After modification with Al2O3 films, the PCE of PSCs increased from 11.72% to 16.08% of the unmodified PCE. A schematic diagram of the surface reorganization inhibition process is shown in Figure 8c. The trap states originating from surface defects in ZnO capture photon-generated electrons and holes, leading to severe recombination. The Al2O3 modification suppresses surface defects, improves the carrier extraction efficiency, and further improves the performance of solar cells. In addition, the thickness of the ALD-Al2O3 film is controlled by the number of ALD cycles. The solar cell performance for different ALD cycles is shown in Figure 8d. The figure shows that the best PCE is obtained when the Al2O3 film has two ALD cycles. Besides inorganic materials, segmented copolymers and poly (ethyleneimine) (PEI) [96,120] have also been used to modify the interface of ZnO and perovskite. These materials generally have larger negative conduction band edges than ZnO. Therefore, once the ZnO surface is covered with these materials, the surface recombination sites are passivated and an energy barrier is formed to prevent photon-injected electrons from approaching the ZnO surface[121].

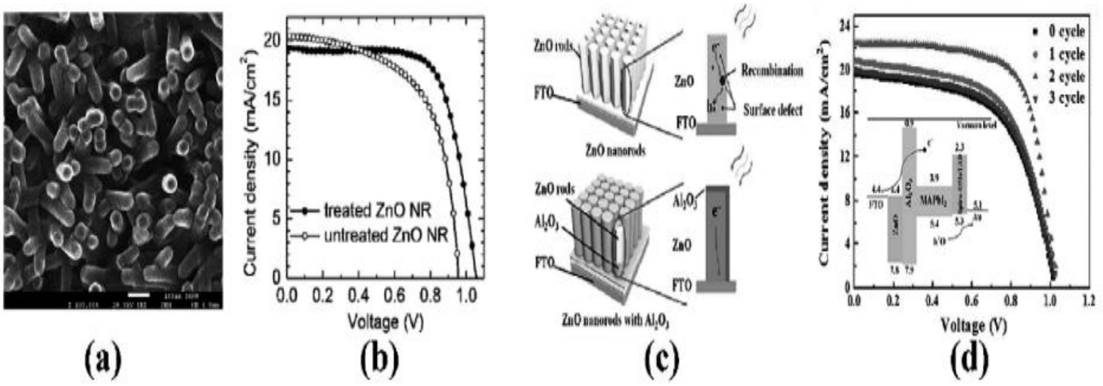


Figure 8: a) The surface morphology of TiO2-modified ZnO nanorods. b) J-V curves of PSCs based on ZnO nanorods with and without TiO2 modification.[92] c) Schematic diagram of surface recombination suppression by Al2O3. d) J-V curves of PSCs with cycles of ALD-Al2O3 on ZnO nanorods; inset: energy band diagram of the PSCs based on ZnO nanorods with Al2O3 coating[119].

Another widely used method to enhance the quality of ZnO-ETM is intentional doping. Dong and colleagues[122] fabricated ultrathin AZO (Al-doped ZnO thin films) on the surface of ZnO nanorods by spin coating. After Al doping, the electrical properties of ZnO are significantly improved, such as higher electron mobility. Z. Tesng and colleagues [56] used AZO instead of intrinsic ZnO thin films as electron transport materials to further improve the efficiency of ZnO-based perovskite solar cells to 17.6%. Mahmood and colleagues fabricated electron-rich nitrogen-doped ZnO nanorods with a PEI capping layer on the surface. In their study, ZnO nanorods were prepared by a hydrothermal method.

To achieve nitrogen doping, ammonium acetate was added to the ZnO nanorod growth solution. In addition, in order to suppress the surface recombination of the ZnO nanorods, the surface of the ZnO nanorods was covered with a PEI film. The PCE of PSC based on the modified ZnO nanorods is 16.1%[96]. Similar results can also be obtained with Mg[123,124], Go[125], Sn[126,127,128],In[129], and Ni[130] doping.

4.2. Poor stability and solutions

Besides recombination, another serious problem is the poor stability of ZnO-based PSCs[131]. When perovskite contacts with ZnO, a deprotonation reaction with methylammonium ions occurs, which is the source of instability, and theoretical calculations confirm this hypothesis.[109] Another important cause of instability is chemical residues from the manufacturing process. According to Yang and colleagues and Cheng and colleagues [109,120] hydroxyl groups and residual acetate in the growth solution exacerbate the decomposition of perovskite. Under the excitation of ultraviolet light, zinc oxide decomposes the perovskite material on its surface. More seriously, the hydroxyl groups and chemical residues on the surface of ZnO could cause photochemical reactions that further accelerate the decomposition of perovskite material[132].

In terms of stability, the reduction of surface defects and surface passivation are also effective to improve the stability of PSCs. After surface passivation, the active zinc oxide surface is covered with TiO2, PEI, [120] Al2O3 or other stable materials, which have been shown to no reaction with perovskite films. Therefore, chemical instability caused by zinc oxide and chemical residues is also avoided. Figure 9a,b shows the XRD patterns of perovskite films on PCBM and PEI-modified ZnO films during annealing. The XRD pattern of the perovskite on the unmodified ZnO film is shown in Figure 9c. It can be seen that for the unmodified ZnO, the perovskite decomposes rapidly after annealing for 30 min. The perovskite on PCBM-modified ZnO remained stable for the first 30 min and began to decompose over time. The perovskite on PEI-modified ZnO remained stable throughout the annealing process. The difference in the stability of the perovskite structure on PEI-modified ZnO and PCBM-modified ZnO is mainly due to the fact that PCBM will aggregate at high temperature, leading to that ZnO is in contact with the perovskite structure again for PCBM-modified ZnO at high temperature.

In addition, especially for solution-treated ZnO-ETMs, high temperature annealing is an effective method to improve the stability of PSCs, but the energy consumption is high. Yang and colleagues [109] and Cheng and colleagues[120] reported methods to improve PSC stability using this method. Figure 9c,d show the XRD patterns of perovskite films annealing on different ZnO films. The perovskite on annealed ZnO shows better stability. In addition, perovskite films can remain stable on AZO films. Figure 9e shows photographs of perovskite films on ZnO films, AZO films fabricated by RF sputtering, and ZnO films fabricated by the sol-gel method. According to Zhao and colleagues[61] and Tseng and colleagues[56,133], AZO films have lower surface basicity than pure ZnO films, thereby improving the stability of perovskite films. As shown in Figure 9f., substituting Al for Zn in AZO can produce Lewis acid sites on the introduced grain surface. In conclusion, the above two methods can inhibit recombination and improve stability simultaneously.

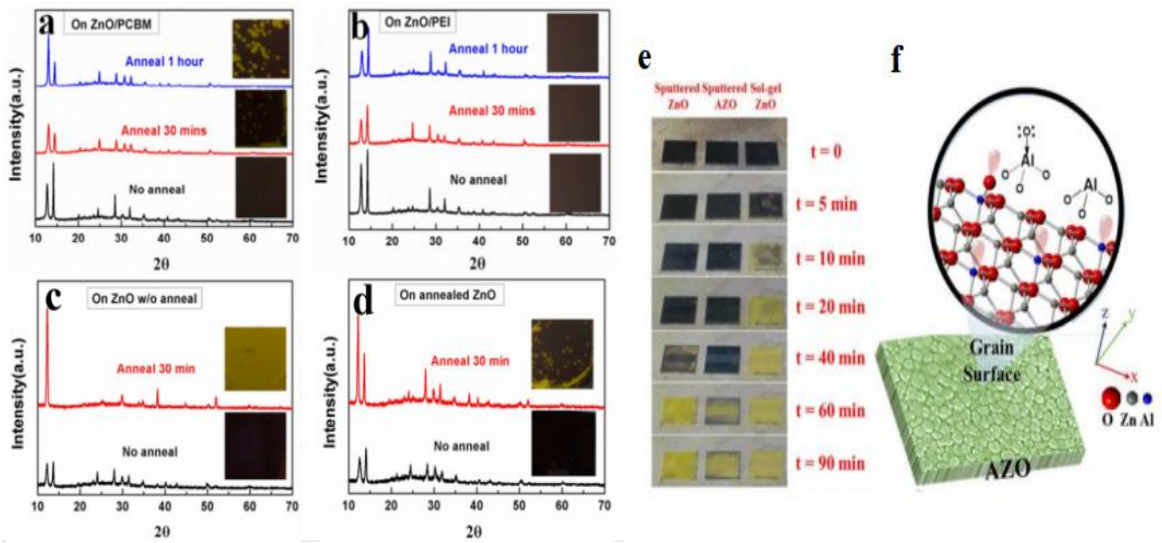


Figure 9: XRD patterns and photographs of perovskite film deposited on PC61BM-coated ZnO[56,120] (a) and PEI-coated ZnO (b) with different thermal annealing treatment; (c) XRD patterns and photographs of perovskite film on ZnO W/O anneal without thermal annealing and annealing at 100°C for 30 min; (d) XRD patterns and photographs ofperovskite film on annealed ZnO without thermal annealing and annealing at 100°C for 30 min.[120](e) The optical images of perovskite films deposited on sputtered ZnO, sputtered Al-doped ZnO (AZO), and sol-gel ZnO. (f) Lewis acid sites on the surface of the grains introduced by replacing Zn with Al in AZO[56].

The metal-organic perovskite materials have poor stability due to the hygroscopicity of organic cations and the weak interaction between organic and inorganic ions.[134] When ZnO is used as the electron transport layer, the problem of instability of MAPbI3 becomes more prominent. The properties of ZnO lead to reverse proton transfer between the interface of ZnO and perovskite, resulting in the decomposition of perovskite into methyl iodide (MAI) and lead iodide (PbI2)[109,135]. Kelly and colleagues found that when using solution-prepared ZnO particles as the electron transport layer, the resulting ZnO/MAPbI3 bilayer was extremely unstable during annealing and easily turned yellow. The alkalinity of ZnO can deprotonate methylamine cations, and But the residual hydroxyl groups and other organic ligands on the surface of ZnO can significantly accelerate the decomposition process. High temperature heating can effectively remove harmful substances on the surface of ZnO, thus significantly improving the thermal stability of MAPbI3 thin films. However, the ZnO electron transport layer heated at high temperature will lead to a sharp drop in the efficiency of perovskite solar cells, and the efficiency of the device after treatment at 400°C is only 7.9%[109].

In order to solve the problem of easy decomposition of MAPbI3 deposited on the ZnO layer prepared by the solution method. Song and colleagues[136] used a ZnO-SnO2 composite material as the electron transport layer, which successfully suppressed the decomposition of MAPbI3. Compared with pure ZnO as electron transport layer, the stability of perovskite film is improved. Tsang and colleagues[120] by introducing a polymer buffer layer between the ZnO and MAPbI3 layers to isolate ZnO and MAPbI3 to prevent their direct contact, the stability of the ZnO/MAPbI3 bilayer was effectively improved, and a PCEs of 10.2% was obtained. Yang Yang's research group, aiming at the instability of ZnO-based devices, used the more stable NiOx as the hole transport layer to prepare a flip-chip perovskite solar cell, as shown in Figure 10a. Figure 10b is a schematic diagram of the corresponding energy band arrangement of the battery. The structure not only improves the device efficiency, achieving a conversion efficiency of 16.1% (Figure 10c), but also effectively improves the device stability. It remained at room temperature for two months and its efficiency remained above 90% of the original efficiency (Figure 10d)[137]. In addition, the choice of cheap NiOx to replace the expensive Spiro-OMeTAD also greatly reduces the fabrication cost of the device, providing a new idea for the preparation of environmentally stable ZnO-based perovskite solar cells in the future, further promoting the development of perovskite solar cells.

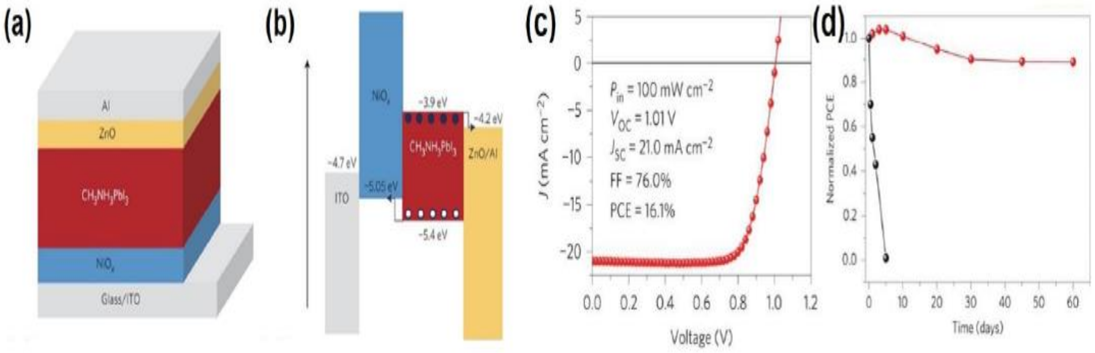


Figure 10: Characterizations of the device with the structure of ITO/NiOx/MAPbI3/ZnO/Al: (a) Structure diagram, (b) energy band alignment and (c) J-V curve; (d) Normalized PCE as a function of storage time (30-50 % humidity)[137].

4.3. Other Methods to Improve Performance

The enhancement of PCE by the surface plasmon effect of metal nanostructures has become an interesting research topic. The introduction of surface plasmon effect can not only improve the light propagating of ZnO thin film ETL, but also improve the efficiency of ZnO-based perovskite solar cells. The introduction of surface plasmon effect in ZnO-based perovskite solar cells will surely improve their photoelectric conversion efficiency. In order to improve the performance of ZnO-based perovskite solar cells, various means need to be further developed to meet the requirements of the practical applications.

5. Conclusion and Outlook

In recent years, the optoelectronic properties of PSCs have been greatly improved. Many novel perovskite compounds and preparation methods have been used to fabricate high-performance solar cells. ZnO materials are widely used in PSCs due to their similar physical properties to TiO_2 but higher electron mobility. In addition, there are many simple methods to prepare ZnO nanomaterials with low cost and low energy consumption. In addition to its excellent properties, ZnO nanomaterials have also been used to fabricate flexible devices due to their abundant preparation methods, which is another important advantage over other materials. Compared with PSCs based on TiO_2 ETM, which is currently the most widely used, PSCs based on ZnO ETM still have poor performance. This is mainly due to serious surface recombination, high defect density and poor stability. In the past few years, a lot of research has been done on these problems and many feasible solutions have been proposed. Optimizing the material quality of ZnO ETM to reduce recombination and improve charge harvesting may still be a research focus. The long-term stability of ZnO ETM perovskite solar cells is another important issue that must be addressed in the coming years. In order to further improve the PCE of perovskite solar cell devices, future research should focus on the following aspects: (1) A dense and high transmittance ZnO electron transport layer should be prepared. The dense ZnO electron transport layer can effectively contact the perovskite active layer, reducing the series resistance. And the high transmittance ZnO thin film can effectively reduce the interface reflectivity and increase the light energy utilization rate of the perovskite light absorbing layer. (2) Doping ZnO with appropriate elements can reduce the defects of the ZnO and improve the electron mobility of ZnO. (3) Selecting suitable inorganic or organic polymer materials to modify ZnO can effectively reduce the surface defects of ZnO films and improve the quality of ZnO films. At the same time, the light transmittance of the electron transport layer can be improved, so as to improve the utilization rate of light energy of the perovskite layer, to further improve the performance of PSCs. (4) Taking the advantage of the low temperature to prepare of ZnO ETM for promoting its application in the flexible devices. (5) Physicochemical treatment of the ZnO ETM layer should be performed to reduce the physicochemical reaction between the ZnO electron transport layer and the perovskite layer, and high-performance PSCs could be obtained.

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