Characterization and Application of Nanomaterials (2021) Volume 4 Issue 2
doi:10.24294/can.v4i2.1324

ORIGINAL RESEARCH ARTICLE

Research progress of nanoarray structure transport layers in perovskite solar cells

Fangxin Tan[1], Shan Cong[1*], Qinghua Yi[1], Zhida Han[1,2], Yushen Liu[1]

[1] *School of Electronic and Information Engineering, Changshu Institute of Technology, Changshu 215500, China. E-mail: congshan@cslg.edu.cn*

[2] *Jiangsu Laboratory of Advanced Functional Materials, Changshu Institute of Technology, Changshu 215500, China*

ABSTRACT

The electron/hole transport layer can promote charge transfer and improve device performance, which is used in perovskite solar cells. The nanoarray structure transport layers can not only further promote carrier transport but also reduce recombination. It also has a great potential in enhancing perovskite light absorption, improving device stability and inhibiting the crack nucleation of different structure layers in perovskite solar cells. This paper reviewed the research progress of perovskite solar cells with different nanoarray structure transport layers. The challenges and development directions of perovskite solar cells based on nanoarray structure transport layers are also summarized and prospected.

Keywords: Perovskite Solar Cells; Nanoarray; Transport Layers

ARTICLE INFO

Received: 5 July 2021
Accepted: 29 August 2021
Available online: 5 Septemper 2021

1. Introduction

Organic-inorganic hybrid perovskite materials have attracted much attention because of their adjustable bandgap, long carrier diffusion length and high light absorption coefficient. They are the preferred materials for solar cells prepared by the low-temperature solution method[1,2]. At present, the certified conversion efficiency of perovskite solar cells (PSC) has exceeded 25%[3]. Conventional perovskite solar cells mainly include planar perovskite solar cells and mesoporous perovskite solar cells. The electron/hole transport layer can accelerate the electron/hole transport in the device and reduce the interface recombination, which plays an important role in improving the efficiency and stability of the device.

At present, various organic and inorganic materials are widely used in perovskite solar cells, such as 2,2', 7,7' -Tetra [N, N-bis (4-methoxyphenyl) amino]-9,9'-Spiro-OMeTAD, poly [bis (4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA), titanium oxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), nickel oxide NiO, and so on[4–7]. the researchers found that the transport layer of nanoarray structure ,such as titanium oxide nanorodarray, zinc oxide nanoarray, not only could promote charge transmission but also reduce interface recombination. It also could enhance perovskite light absorption, inhibit crack nucleation of different structural layers in perovskite solar cells, and improve the stability of flexible devices[8–10]. This paper introduces the research progress at home and abroad, which includes the design and preparation of nanoarray structures of different electron and hole transport layer materials.

2. Research progress of nanoarray electron transport layer

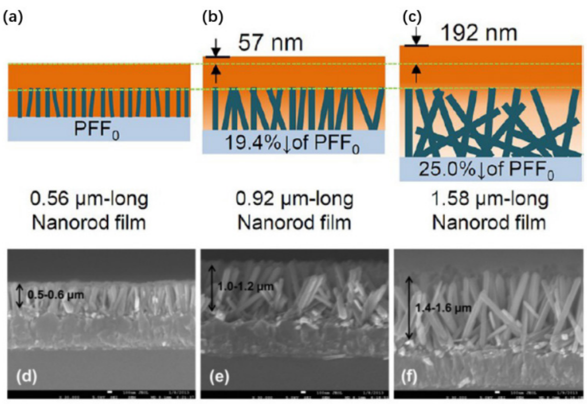
2.1 Metal oxide nanoarrays

The electron transport layer materials of a metal oxide represented by TiO_2, ZnO, and SnO_2, are widely used in perovskite solar cells, photodetectors and other optoelectronic devices with their excellent electron transport capacity, relatively good environmental stability and convenient preparation process[11–14].

2.1.1 Titanium oxide TiO_2

TiO_2 is easy to prepare, low-cost, with appropriate energy level and electron transport capacity. PSC use TiO_2 as an electron transport layer material widely. At present, the research on TiO_2 nanoarray mainly focuses on the preparation method and structural composition to optimize its performance and structure. It improve electron transport efficiency using TiO_2 nanoarray, reduces interfacial recombination, enhances the light absorption of photoactive layer, playing a good role in improving the stability of the device.

Kim *et al.* reported an efficient perovskite solar cell using submicron (~0.6 μm) rutile TiO_2[15]. TiO_2 nanorods were grown by hydrothermal method, and



(a) ~ **(c)** effect of different TiO_2 nano array height on device performance; **(d)** ~ **(f)** scanning electron microscope images of different TiO_2 nano array heights[15].

Figure 1. Application of TiO_2 nanoarray.

the reaction time adjusted the length of nanorods. Experiments showed that the current density would decrease due to the increase of nanorods. It is mainly due to the tilt of the nanorods during the growth process, which affects the filling of perovskite and ultimately affects the device efficiency (**Figure 1**).

Huh *et al.* enhanced the performance of PSC by selectively growing TiO_2 nanorods[16]. They selectively grew TiO_2 nanorod substrate by nanoimprint lithography and hydrothermal growth method. Experiments show that TiO_2 nanorods, as an electron transmission channel, can effectively improve the electron-hole separation energy, reduce interface recombination, and obtain an open circuit voltage of 1.12 V. In addition, TiO_2 nanorods can increase the optical path of the incident light, enhance the light absorption of the active layer and improve the device performance.

Hu *et al.* prepared a TiO_2 nano column array by grazing angle deposition[17]. Scanning electron microscope studied The TiO_2 nano column array, scanning near-field optical microscope, and UV-Vis absorption. It found that the TiO_2 nano column transport layer can enhance the optical absorption of perovskite through a large number of precursor penetration paths, near-field light concentration, and partial UV shielding. Thus it improves the short circuit current and stability of the device.

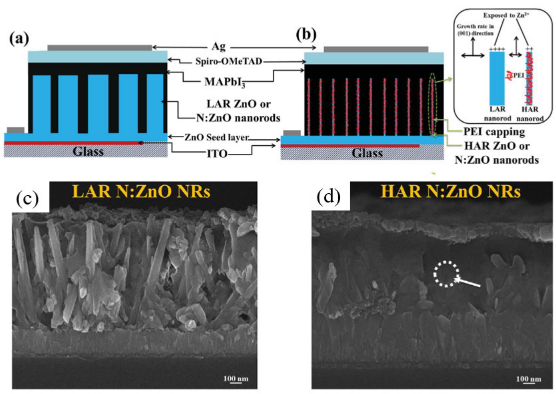
Liu *et al.* deposited the optimized CdS shell on TiO_2 nanoarray at room temperature by a simple chemical bath method, which significantly improved the efficiency and stability of PSCs[18]. Experiments show that, on the one hand, the CdS shell can passivate oxygen vacancies on the TiO_2 surface, prevent electron-hole recombination and protect the calcium titanium layer. On the other hand, the insertion of Cds shell on the surface of TiO_2 is helpful to form a type-II structure, which can further accelerate electron transfer and the Cds@TiO_2 coaxial nanoarray structure provides enough space for perovskite implantation. Xiao *et al.* successfully doped Nb in titanium oxide array by hydrothermal method[19]. The research shows that in the interface between TiO_2 and perovskite, TiO_2 doped with Nb is more efficient for electron transport and charge separation, which provides an effective way to prepare PSCs with high performance and high stability.

2.1.2 Zinc oxide ZnO

Similar to TiO_2, ZnO is also a common electron transport material in perovskite solar cells. Its electron mobility is higher than TiO_2, and it is more controllable jn form and has a lower synthesis temperature. These advantages make it widely used in PSC[20,21]. At present, the research on ZnO nanoarrays mainly focuses on many ways, such as how to improve preparation methods,interface modification, increase perovskite filling, reduce carrier recombination as well as improve device efficiency.

Tulus *et al.* Deposited gold nanoparticles on the surface of ZnO nanorod array using vacuum deposition technology to increase the hole Schottky barrier at the interface of ZnO perovskite active layer, as shown in **Figure 2(a)**. Further block holes, passivate carrier composite defects on the surface of ZnO nanorods, reduce the loss of open-circuit voltage of devices, and improve the filling factor, thus, the conversion efficiency of the battery improved[22].

Dong *et al.* doped the ZnO nanorod array with Al and formed an Al-Zn-O layer on the surface of the ZnO nanorod. While passivating the surface defects of the ZnO nanorod, they also adjusted the energy level to make the energy level of the active layer better match that of the electron transport layer, improve the electron transport efficiency, and finally improve the device[23].



(a) device structure diagram of conventional low aspect ratio (LAR) ZnO nanoarrays and **(b)** high aspect ratio (HAR) ZnO nanoarrays with PEI coating (illustration: PEI as a capping agent for controlling nanotube growth); based on the scanning electron microscope cross-sectional images of 1,070 nm intact cells of LAR N: ZnO NRs **(c)** and HAR N: ZnO NRs **(d)** without PEI coating, the results show that HARZnO nanoarrays have better perovskite wetting properties[24].

Figure 2. Application of ZnO nanoarrays.

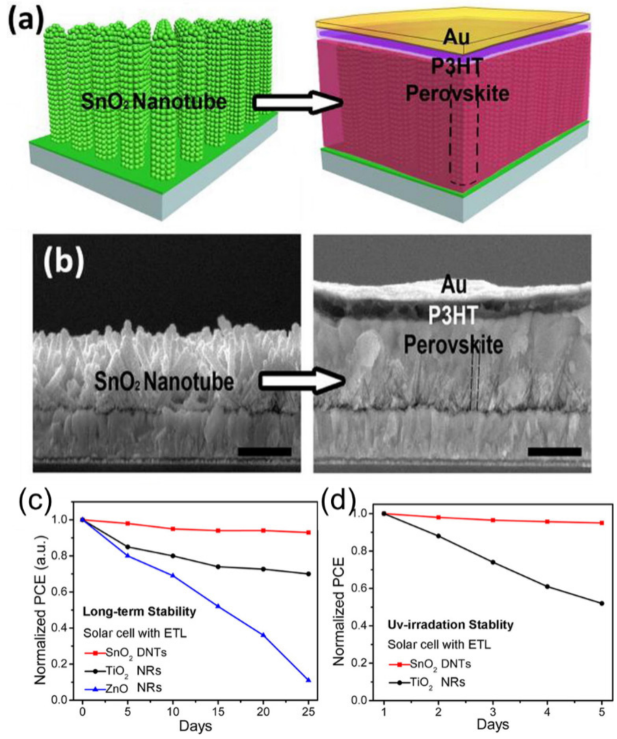
Mahmood *et al.* combined with the dual characteristics of polyethyleneimine (PEI) as dipole layer and selective polymer cover, prepared N: ZnO nanoarrays with high aspect ratio and electron-rich nitrogen doping through low-temperature solution-phase hydrothermal growth[24]. Then he applied them in PSC to effectively improve the penetration of calcium titanium ore in the array, inhibit carrier recombination and improve device efficiency (**Figure 2**). At the same time, they successfully applied PEI coating on the N: ZnO array adjusted the work function, and obtained stable and hysteresis-free devices with device efficiency > 16%.

More interestingly, Zhao *et al.* prepared highly ordered ZnO nanorod arrays at low temperatures (90°C)[25]. This nanoarray structure has excellent mechanical stability when combined with a flexible substrate, and its performance remains 90% after 1,000 bending cycles with a radius of curvature of 4 mm. It has excellent bending resistance and durability and has great application potential in foldable photovoltaic devices.

2.1.3 Stannic oxide SnO_2

In recent years, planar PSCs with SnO_2 ETLs have developed rapidly due to the excellent characteristics of SnO_2 materials, such as appropriate energy level, high electron mobility, good transmittance, excellent chemical stability, and inactive UV catalysis. Similar to zinc oxide, stannic oxide also faces many problems of morphology and defect states. Optimize the stannic oxide nanorod arrays using the same passivation strategy[26].

Song *et al.* doped SnO_2 nanocrystals with Y^{3+} by typical solvothermal method[27]. The results show that Y dopant has a more appropriate energy level structure and better carrier dynamics performance, and obtains devices with a total efficiency of 20.71%. Gao *et al.* proposed an effective in-situ template self-etching method on the basis of a series of controllable experiments, stannic oxide nanotube arrays were prepared with zinc oxide nanorods as sacrificial templates, and the growth mechanism of nanotubes was studied[28]. By comparing stannic oxide nanotube array PSC devices with similar SnO_2 or ZnO PSCs, PSC with stannic oxide nanotube array as transport layer has better long-term stability and UV stability (**Figure 3**). This work emphasizes the importance of the material selection of an electron transport layer and provides an idea for realizing ideal electron transport layer/substrate homogeneous junction to promote electron transport.



(a) schematic diagram based on SnO_2 nanoarray and its devices; **(b)** the corresponding scanning electron microscope cross-sectional image, with a scale of 500 nm; **(c)** comparison diagram of long-term stability based on SnO_2, TiO_2, and ZnO nanoarrays; **(d)** based on the UV stability comparison diagram of SnO_2 and TiO_2 nanoarray perovskite solar cells, the results show that SnO_2 nanoarray perovskite solar cells have better stability[28].

Figure 3. Application of SnO_2 nanoarray.

2.2 Other nanoarray electron transport materials

Through previous work, it finds that zinc compounds usually have excellent electrical properties. so it is also an important topic to develop the electron transport layer materials of zinc compound. Tavakoli *et al.* introduced Zn_2SnO_4 nanorod array as electron transport layer into perovskite solar cells, although the short-circuit current of the obtained devices increased and the hysteresis significantly reduced. However, the open-circuit voltage loss caused by energy level mismatch still needs to solve[29].

3. Research progress of hole transport layer of nanoarray

The hole transport materials commonly used in PSC mainly include organic materials and inorganic hole transport materials. These holes materials need to meet the conditions of good hole transport capacity, high stability, and matching with perovskite energy level. Organic hole transport materials, such as polyethylene dioxythiophene-poly(styrene sulfonate) (PEDOT: PSS), poly[bis (4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA), are of relatively complex synthesis, and it is not easy to prepare nanorod array structure. In addition, the acidity of PEDOT: PSS and the instability of unsaturated carbon bonds in organic materials are not conducive to the long-term stable operation of the device. The preparation process of inorganic hole transport materials, such as nickel oxide NiO, cuprous iodide CuI, cuprous thiocyanate CuSCN, is relatively simple and convenient structural regulation[30–32].

Gan *et al.* successfully synthesized CuSCN nanorod arrays with good crystallinity and electrical properties at room temperature by adjusting the synthesis temperature and deposition potential, which opened an opportunity for their application in the field of optoelectronic devices[33]. Xi *et al.* applied CuSCN nanowire array and its similar derived microstructure to perovskite solar cells to achieve a photoelectric conversion efficiency of more than 7.5%. At the same time, the research results show that the introduction of CuSCN nanowire array and its derived microstructure is conducive to obtaining a more regular perovskite active layer interface, improving the crystal orientation of perovskite and reducing crystal defects at the active layer and interface, reducing carrier recombination and improving device performance[34].

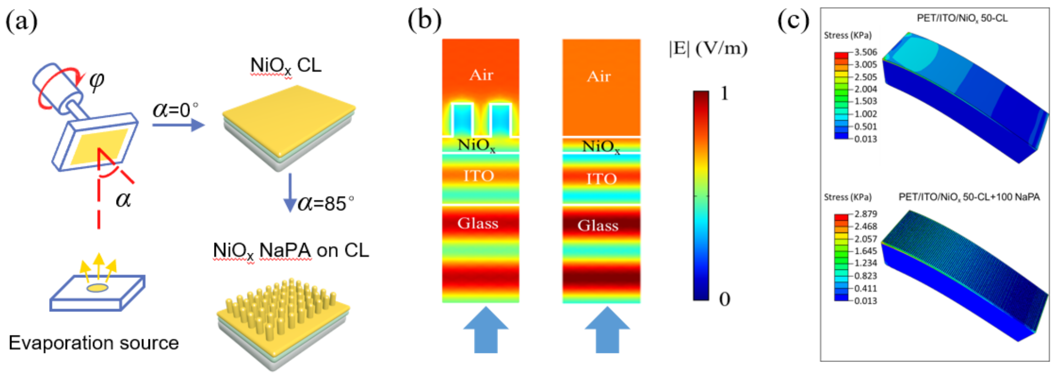
Anandan *et al.* introduced the wet prepared CuO nanorod array into the dye-sensitized solar cell and obtained a cell with 0.29% conversion efficiency, which proved that the CuO nanorod array could be used as the photoanode (hole transport layer) of the dye-sensitized solar cell. But the CuO band gap was small (about 1.2 eV), such natural defect makes it impossible to completely separate photogenerated electron-hole pairs, resulting in the recombination of a large number of carriers at the CuO interface, affecting the efficiency of the device and greatly limiting its application[35].

Cong *et al.* prepared well-crystallized nickel oxide nanorod arrays at room temperature by grazing angle deposition. It proved that the introduction of nickel oxide arrays reduced the reflection of the light incident surface, increased the light capture of the device, passivated the interface defects between the hole layer and the active layer, induced perovskite crystal growth, obtained high-quality perovskite films, and finally obtained more than 20% photoelectric conversion efficiency. At the same time, the advantages of low-temperature preparation make this structure also have a conversion efficiency of more than 17% on the flexible substrate. Moreover, due to the mesoporous structure of the array, the device stress is relieved and the stable operation of the devices on the flexible substrate is guaranteed, which proves the application potential of nanorod array in flexible devices[36] (**Figure 4**).

Zheng *et al.* introduced copper phthalocyanine (CuPc) nanorod arrays into organic solar cells. Through close engagement with PCBM molecules in the active layer, the dark current intensity of the device reduces, and the device performance is doubled compared with the device based on planar CuPc structure. It also shows that this structure can effectively passivate the defects between the active layer and the electrode[37]. Zhang shows that it can effectively replace the current mainstream Spiro-OMeTAD hole transport materials doped with a lithium salt, which integrates the undoped CuPc nanorod array with the electrode from the perspective of chemical stability. And obtain a battery with high repeatability with an efficiency of 16.1%[38].

4. Conclusion

This paper describes the application and research progress of nanoarray transport layer materials in PSC. Generally, these devices mainly focus on the preparation and optimization of oxide materials. The preparation methods are a popular such as hydrothermal method, vacuum deposition, template method. Generally, the devices with nanoarray transport layer materials can improve the carrier transport efficiency, and enhance the absorption of the photoactive layer. At present, most of the devices prepared by these materials are still small-area devices based on a glass substrate. There is still great potential in the preparation of flexible devices and large-area de-



(a) grazing angle deposition of NiO nanoarrays; **(b)** the finite element analysis of the electric field distribution diagram with/without NiO nanoarray substrate. The results show that NiO nanoarray structure is conducive to increasing light transmission and reducing light reflection; **(c)** the finite element analysis stress distribution diagramof the flexible substrate with/without NiO nanoarray.The results show that the NiO nanoarray structure has better bending resistance[36].

Figure 4. Application of NiO nanoarrays.

vices. In the future, it is necessary to select appropriate flexible substrates for the high-quality growth of nanoarrays through interface modification or doping to improve the carrier mobility, reduce the carrier recombination, improve the device stability, and realize the preparation and application of flexible wearable devices.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

Project: The National Natural Science Foundation of China Project "Study on stability mechanism of perovskite solar cells based on NiO nano arrays" (62005027); Jiangsu Natural Science Foundation Project "Growth of efficient and stable TiO_2 array @(rGO/Cu_2O) heterojunction electrode by polymer assisted deposition and its photoelectrochemical hydrolysis mechanism" (BK20181037).

References

1. Kim HS, Lee CR, Im JH, *et al.* Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. Scientific Reports 2012; 2(1): 591.
2. Chen Q, Zhou H, Hong Z, *et al.* Planar heterojunction perovskite solar cells via vapor-assisted solution process. Journal of the American Chemical Society 2014; 136(2): 622–625.
3. Ma C, Park NG. A realistic methodology for 30% efficient perovskite solar cells. Chemistry 2020; 6(6): 1254–1264.
4. Kung PK, Li MH, Lin PY, *et al.* A review of inorganic hole transport materials for perovskite solar cells. Advanced Materials Interfaces 2018; 5(22): 1800882.
5. Shin SS, Suk JH, Kang BJ, *et al.* Energy-level engineering of the electron transporting layer for improving open-circuit voltage in dye and perovskite-based solar cells. Energy and Environmental Science 2019; (12): 958–964.
6. Tan B, Raga SR, Chesman ASR, *et al.* LiTFSI-free Spiro-OMeTAD-based perovskite solar cells with power conversion efficiencies exceeding 19%. Advanced Energy Materials 2019; 9(32): 1901519.1–1901519.10.
7. Tang G, You P, Tsi Q, *et al.* Solution-phase epitaxial growth of perovskite films on 2D material flakes for high-performance solar cells. Advanced Materials 2019; 31(24): e1807689.
8. Huh D, Oh KS, Kim M, *et al.* Selectively patterned TiO_2 nanorods as electron transport pathway for high performance perovskite solar cells. Nano Research 2019; 12(3): 601–606.
9. Lv Y, Wang P, Cai B, *et al.* Facile fabrication of SnO_2 nanorod arrays films as electron transporting layer for perovskite solar cells. Solar RRL 2018; 2(9): 1800133.
10. Sun J, Hua Q, Zhou R, *et al.* Piezo-phototronic effect enhanced efficient flexible perovskite solar cells. ACS Nano 2019; 13(4): 4507–4513.
11. Boro B, Gogoi, B, Rajbongshi, BM, *et al.* Nano-structured TiO_2/ZnO nanocomposite for dye-sensitized solar cells application: A review. Renewable and Sustainable Energy Reviews 2018; 81(2): 2264–2270.
12. Zhang P, Wu J, Zhang T, *et al.* Perovskite solar cells with ZnO electron-transporting materials. Advanced Materials 2018; 30(3): 1703737.
13. Jiang Q, Zhang X, You J. SnO_2: A wonderful electron transport layer for perovskite solar cells. Small 2018; 14(31): 1801154-1–1801154-14.
14. Seo JY, Uchida R, Kim HS, *et al.* Boosting the efficiency of perovskite solar cells with CsBr-modified mesoporous TiO_2 beads as electron-selective contact. Advanced Functional Materials 2018; 28(15): 1705763.
15. Kim HS, Lee JW, Yantrar N, *et al.* High efficiency solid-state sensitized solar cell-based on submicrometer rutile TiO_2 nanorod and $CH_3NH_3PbI_3$ perovskite sensitizer. Nano Letters 2013; 13(6): 2412–2417.
16. Huh D, Oh K, Kim M, *et al.* Selectively patterned TiO_2 nanorods as electron transport pathway for high performance perovskite solar cells. Nano Research 2019; 12(3): 601–606.
17. Hu Z, García-Martín JM, Li Y, *et al.* TiO_2 nanocolumn arrays for more efficient and stable perovskite solar cells. ACS Applied Materials & Interfaces

2020; 12(5): 5979–5989.
18. Liu W, Chu L, Liu N, *et al.* Simultaneously enhanced efficiency and stability of perovskite solar cells with TiO_2@CdS core-shell nanorods electron transport layer. Advanced Materials Interfaces 2019; 6(5): 1801976.
19. Xiao G, Shiu C, Lv K, *et al.* Nb-doping TiO_2 electron transporting layer for efficient perovskite solar cells. ACS Applied Materials & Interfaces 2018; 1(6): 2576–2581.
20. Bi D, Boschloo G, Schwarzmüller S, *et al.* Efficient and stable CH3NH3PbI3-sensitized ZnO nanorod array solid-state solar cells. Nanoscale 2013; 5(23): 11686–11691.
21. Liu D, Wang Y, She Z, *et al.* Suppressed decomposition of perovskite film on ZnO via a self-assembly monolayer of methoxysilane. Sol RRL 2018; 2(12): 1800240.
22. Tulus, Olthof S, Marszalek M, *et al.* Control of surface defects in ZnO nanorod arrays with thermally-deposited au nanoparticles for perovskite photovoltaics. ACS Applied Energy Materials 2019; 2(5): 3736–3748.
23. Dong J, Zhao Y, Shi J, *et al.* Impressive enhancement in the cell performance of ZnO nanorod-based perovskite solar cells with Al-doped ZnO interfacial modification. Chemical Communications 2014; 50(87): 13381–13384.
24. Mahmood K, Swain BS, Amassian A. 16.1% efficient hysteresis-free mesostructured perovskite solar cells based on synergistically improved ZnO nanorod arrays. Advanced Energy Materials 2015; 5(17): 1500568.
25. Zhao X, She H, Sun R, *et al.* Bending durable and recyclable mesostructured perovskite solar cells based on superaligned ZnO nanorod electrode. Sol RRL 2018; 2(5): 1700194.
26. Liu D, Wang Y, Xu H, *et al.* SnO_2-based perovskite solar cells: Configuration design and performance improvement. Sol RRL 2019; 3(2): 1800292.
27. Song J, Zhang W, Wang D, *et al.* Colloidal synthesis of Y-doped SnO_2 nanocrystals for efficient and slight hysteresis planarsperovskite solar cells. Solar Energy 2019; 185: 508–515.
28. Gao C, Yuan S, Cao B, *et al.* SnO_2 nanotube arrays grown via an in situ template-etching strategy for effective and stable perovskite solar cells. Chemical Engineering Journal 2017; 325: 378–385.
29. Tavakoli MM, Prochowicz D, Yadav P, *et al.* Zinc stannate nanorod as an electron transporting layer for highly efficient and hysteresis-less perovskite solar cells. Engineered Science 2018; 3: 48–53.
30. Pattanasattayavong P, Yaacobi-Gross N, Zhao K, *et al.* Hole-transporting transistors and circuits based on the transparent inorganic semiconductor copper (I) thiocyanate (CuSCN) processed from solution at room temperature. Advanced Materials 2013; 25(10): 1504–1509.
31. Truong NTN, Hoang HHT, Park C. Improvement of vacuum free hybrid photovoltaic performance based on a well-aligned ZnO nanorod and WO_3 as a carrier transport layer. Materials 2019; 12(9): 1490.
32. Boix PP, Larramona G, Jacob A, *et al.* Hole transport and recombination in all-solid Sb2S3-sensitized TiO_2 solar cells using CuSCN as hole transporter. Journal of Physical Chemistry C 2011; 116(1): 1579–1587.
33. Gan X, Liu K, Du X, *et al.* Bath temperature and deposition potential dependences of CuSCN nanorod arrays prepared by electrochemical deposition. Journal of Materials Science 2015; 50(24): 7866–7874.
34. Xi Q, Gao G, Zhou H, *et al.* Highly efficient inverted solar cells based on perovskite grown nanostructures mediated by CuSCN. Nanoscale 2017; 9(18): 6136–6144.
35. Anandan S, Wen X, Yang S. Room temperature growth of CuO nanorod arrays on copper and their application as a cathode in dye-sensitized solar cells. Materials Chemistry and Physics 2005; 93(1): 35–40.
36. Cong S, Zou G, Lou Y, *et al.* Fabrication of nickel oxide nanopillar arrays on flexible electrodes for highly efficient perovskite solar cells. Nano Letters 2019; 19(6): 3676–3683.
37. Zheng Y, Bekele R, Ouyang J, *et al.* Organic photovoltaic cells with vertically aligned crystalline molecular nanorods. Organic Electronics 2009; 10(8): 1621–1625.
38. Zhang F, Yang X, Cheng M, *et al.* Boosting the efficiency and the stability of low cost perovskite solar cells by using CuPc nanorods as hole transport material and carbon as counter electrode. Nano Energy 2016; 20: 108–116.