Design strategies of ZnO heterojunction arrays towards effective photovoltaic applications

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Abstract
ZnO nanorods (NRs) heterojunction arrays have been widely used in photovoltaic cells owing to the outstanding photoelectrical characteristics, high stability and low cost. The NRs arrays structure can integrate multiple functional components, so that it can exhibit more excellent physical and chemical properties that even independent components do not possess. The design of heterojunction nanostructures can effectively solve the problems of light absorption and carrier transport. First, the synthesis methods of ZnO NRs and their heterojunction arrays were systematically introduced, including traditional chemical vapor deposition (CVD), electrodeposition, hydrothermal method, and so on, the different structures and properties of ZnO NRs heterojunctions were analyzed. Then, the selected materials could be further processed and assembled into NRs array heterojunction with integrated functions were discussed. The strategies of maximizing energy conversion performance (structure optimization, heterojunction, surface plasmon resonance, and doping) were emphatically summarized. In addition, the research progress of ZnO NRs and their heterojunctions in photoelectric energy conversion system were summarized, and the application potential of combining nanostructure design with solar cells was summarized. Finally, the challenges and future development prospects of ZnO NRs and their heterojunction arrays in photovoltaic conversion were pointed out.

KEYWORDS
heterojunction array, preparation method, solar cell, ZnO NRs

1 INTRODUCTION

ZnO nanorods (NRs) have become the most researched inorganic materials in the field of solar cells due to their high aspect ratio, large specific surface area, high electron mobility, and good single crystal properties.1–8 However, the disordered arrangement of NRs will lead to poor carrier transport performance, which will become one of the reasons restricting the low efficiency of solar cells. The orderly arrangement of NRs on the substrate has better photoelectrical performance than the randomly stacked NRs.9–13 Therefore, researchers hope to improve the efficiency of

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carrier transport and optimize the photoelectric performance of solar cells by constructing NRs array structures. In particular, the construction of ZnO NRs arrays provides high-speed channels for the transport of electrons with less grain boundaries, thereby effectively promoting the separation of electrons and holes. In addition, when the incident light is scattered among NRs, the light absorption of the materials can be improved. Compared with ZnO nanoparticles (NPs), ZnO NRs arrays have obvious advantages in the process of photo-generated carriers transport. At present, the preparation methods of ZnO NRs arrays mainly include chemical vapor deposition (CVD),37 microwave method,23,24 hydrothermal method,25–35 low-temperature oxidation method,36 electrodeposition method,37–41 and other methods.45–56 However, ZnO as a semiconductor oxide with wide band gap (~3.2 eV), which limits its utilization of light. Therefore, by introducing the heterojunction array structure, the carrier separation channel is increased by the interface area of the heterojunction, thereby improving the carrier separation and collection efficiency. Among them, using ZnO NRs array structure to construct the radial heterostructure can reduce the separation distance of carriers without sacrificing the light absorption of ZnO, so as to improve the transport efficiency of photogenerated carriers, which has become the first strategy to improve the photoelectric performance of ZnO-based solar cells. For example, ZnS,57–60 TiO2,61,62 Cu2O,63,64 and graphene65–68 were combined with ZnO NRs to construct heterostructures and broaden the light absorption range of ZnO. With the aid of interface heterojunction materials of the two materials, it shows more obvious quantum effect and two-dimensional characteristics. With these characteristics, the heterostructures have been widely used in solar cell materials in recent years. In this paper, the preparation methods of ZnO NRs arrays and the research of heterojunction materials in the field of solar cells were reviewed. First, the strategy of regulating ZnO NRs synthesis route, growth conditions, and construction of heterostructures were introduced. Subsequently, the application and photoelectric performance of ZnO NRs arrays in solar cells were emphatically introduced. Finally, the shortcomings of ZnO NRs arrays and their heterojunction materials in the field of solar cells were pointed out, and their future development prospects were prospected.

2 | SYNTHESIS OF ZnO NRs ARRAYS

2.1 | Chemical vapor deposition

As a widely used method for preparing ZnO NRs developed in recent decades, NRs arrays synthesized by CVD method have been reported successively.70–74 That is, the steam is placed under the catalyst, so that the seed layer is concentrated until saturated in the steam. At this time, the steam reacts on the substrate, and the target product gradually solidifies and grows from the catalyst. In addition, Song et al.75 found that oxygen content is an important factor affecting the structure of ZnO NRs when other growth conditions are controlled unchanged. By controlling oxygen content, the morphology of ZnO NRs arrays can be optimized.

ZnO NRs can be grown by metal-organic chemical vapor deposition (MOCVD) method. The size and orientation of NRs are also related to the substrate type. For example, Hassan et al.76 prepared ZnO NRs arrays on silicon and GaN substrates by MOCVD method. It was found that ZnO NRs grown on silicon substrates had tapered tips, these NRs were randomly arranged and inclined relative to the normal line of silicon substrate surface (Figure 1A, B). The reason is that silicon and ZnO belong to different crystal structures, and there is a large lattice mismatch between them. However, ZnO NRs grown on GaN were well arranged. Most of NRs were perpendicular to the GaN substrate and have relatively uniform NRs in length, diameter, distribution, and height (Figure 1C, D).

To improve the vertical orientation of NRs, the seed layer can be introduced to reduce lattice mismatch, it has become a common strategy to adjust the growth position of NRs by using the ZnO seed layer as the active nucleus for the growth of NRs. Compared with the traditional CVD, plasma enhanced chemical vapor deposition (PECVD) can not only achieve conformal deposition on surfaces with complex shapes, but also complete the synthesis of nanostructures on substrates at low temperatures. Since in the process of PECVD, NPs were not needed as catalysts, which simplifies the preparation process while avoiding the entry of metal impurities. Bekermann et al. prepared high-purity and well-arranged ZnO NRs on silicon substrates at 200–300°C using PECVD.77 Well-arranged single crystal ZnO NRs on GaAs substrates using MOCVD were grown. This method can also be used to prepare ZnO NRs by changing the relevant experimental conditions.78

2.2 | Electrochemical deposition

Electrochemical deposition can precisely control the thickness, chemical composition, and structure of the deposited layer on different substrates by controlling the electrodeposition parameters. With its advantages of low cost, simple operation, and time-saving, it has become another way to prepare ZnO NRs arrays.79–91 The electrochemical deposition of ZnO NRs consists of two processes: nucleation and growth of crystal. The
nucleation rate and growth rate directly affect the density and length of ZnO NRs, respectively. When the nucleation rate is faster, the density of ZnO NRs will increase. When the growth rate is relatively fast, the length of ZnO NRs will increase. The concentration of Zn$^{2+}$ precursor, electrodeposition time, electrolyte concentration, and temperature also have important effects on NRs arrays. Usually, high concentration of Zn$^{2+}$ precursors will lead to high nucleation rate. The height of ZnO NRs is mainly affected by the electrodeposition time and the concentration of electrolyte.\cite{92} The higher the electrolyte concentration, the morphology of ZnO will change from rod-like to lamellar.

The higher the electrodeposition temperature, the greater the density of ZnO prepared by electrodeposition, the more uniform the size, and the significantly improved crystalline quality. The increase in electrodeposition voltage not only increases the density of ZnO, but also increases the preferred orientation of the c-axis and improves the crystal quality. Appropriate voltage can form ZnO NRs with good morphology, while too high a voltage will cause the ZnO NRs to transform into a cluster structure.\cite{93} When the deposition time is very short, thin and short NRs are formed. As the deposition time increases, the length and diameter of ZnO NRs increase, and the coalescence between adjacent NRs effectively reduces the packing density of NRs.\cite{94,95} Skompska et al. comprehensively analyzed the influence of Zn$^{2+}$ and OH$^{-}$ precursor types, as well as different adjustment strategies for ZnO nanostructure shapes.\cite{96} Meng et al. prepared ZnO NRs with NPs attached on the surface by two-step electrochemical deposition method. ZnO NRs arrays were first prepared on FTO substrates by simple electrochemical deposition, and then the NRs arrays were placed in zinc acetate solution for secondary deposition to obtain ZnO NRs arrays wrapped by nanoparticles.\cite{97} ZnO NRs were obtained by primary electrodeposition (Figure 2A), and then the electrochemical epitaxial growth of two-layer (Figure 2B,C) or six-layer NRs (Figure 2D) was directed onto the primary nanostructures.\cite{98}

Compared with constant current, pulse electrodeposition can promote the formation of nuclei and other fine grains. By changing cycle time, pulse frequency and duty cycle, ZnO NRs arrays can be prepared through potential pulse electrodeposition, and high density ZnO NRs arrays can be prepared through constant potential-static pulse electrodeposition method.\cite{99}

2.3 | Hydrothermal method

CVD and electrodeposition methods usually require precise instruments and strict experimental conditions.
As another process for large-scale synthesis of ordered ZnO NRs arrays, hydrothermal method has the advantages of low cost, low temperature preparation, and simple and controllable process. In the hydrothermal process, the selection of zinc precursor and alkali source is particularly important. The zinc precursor usually uses zinc nitrate and zinc acetate. The two commonly used alkali sources are ammonia and hexamethylenetetramine (HMT). It was found that the size, surface density, and distribution of NRs can be adjusted by changing substrate type, precursor, heating time, and temperature. To overcome the lattice mismatch, a seed layer is usually grown on the surface of substrate before growing ZnO NRs with hydrothermal reaction. Vayssieres et al. prepared highly oriented ZnO NRs on conductive glass using zinc nitrate and HMT solution. Vayssieres et al. succeeded in reducing the diameter of NRs to 100–200 nm by keeping the ratio of Zn$^{2+}$ to amine at 1:1. Greene et al. explored the morphology and photoluminescence properties of ZnO NRs by synthesizing materials on different substrates. Xu et al. found that high-quality ZnO NRs arrays can also be grown by choosing Zn(C$_2$H$_3$O$_2$)$_2$ and CH$_3$N$_2$O as precursors, and alkali sources of zinc, respectively. Compared with other synthesis routes, the quality of the material prepared by hydrothermal method has declined, and some NRs will deviate from the normal direction of substrate during the growth process. It has also become the development trend to prepare ZnO NRs arrays by other methods assisted hydrothermal method. Fang et al. prepared ZnO seed layer by magnetron sputtering technology, and then successfully synthesized (002) orientated ZnO NRs arrays on silicon substrate by microwave-assisted hydrothermal method. In addition, the diameter distribution of ZnO NRs prepared by hydrothermal method is also wider. Therefore, how to better control the morphology, growth density and diameter distribution of ZnO NRs are still problems to be solved in the process of hydrothermal preparation. Zhang et al. first produced patterned zinc oxide seed regions of different sizes on silicon substrates through e-beam lithography (EBL), and explored the morphology and growth mechanism of NRs arrays. Then, ZnO NRs arrays with different morphologies and densities were prepared on silicon substrates with high precision by hydrothermal method (Figure 3A–D). This study provides a favorable guidance for the application of integrated preparation of NRs devices based on ZnO NRs arrays.

Kim et al. prepared three different patterned ZnO seed layers by nanolithography (Figure 4A–C), and
controlled the thickness and exposed area of ZnO seed layers by regulating the polymethyl methacrylate (PMMA) mask layer and the etching time, and then precisely arranged ZnO NRs was prepared by hydrothermal growth method (Figure 4D–F), this highly regular ZnO NRs arrays integrates the excellent optical and electrical properties of ZnO.\textsuperscript{107}

From the perspective of structural design and the application of solar cells, the selection of low-cost and large-scale growing preparation methods become two factors to be considered. Cheng et al. first prepared ZnO NRs arrays on FTO glass (Figure 5A,B), then through the growth of ZnO seed layers coated on NRs arrays (Figure 5C), and the branching ZnO nanostructures (Figure 5D) were prepared, which were directly connected to the main chain of ZnO NRs and could provide a direct path of carriers transport.\textsuperscript{108}

In addition to the above common synthesis methods, there are many other methods to prepare ZnO NRs arrays, such as chemical bath deposition (CBD), sol–gel methods and spray pyrolysis, and so on.

3 | SYNTHESIS OF ZnO NRs HETEROJUNCTION ARRAYS

Although ZnO NRs array provide a direct carrier transport channel, its wide band gap leads to low photovoltaic conversion efficiency (PCE) based on ZnO NRs arrays. Therefore, the construction of heterojunction on ZnO NRs can improve the light capture ability and increase the transport properties. The heterojunction and plasma metal NPs modification are two main forms. Hierarchical structure and core-shell structure are widely used in heterostructures.\textsuperscript{109} The hierarchical structure usually covers the composite material on the original material, the prominent feature of the core-shell structure is to increase the photocurrent density. In addition, the shell layer as an energy barrier, it can also reduce the loss caused by electron recombination, and make the conduction band move down to increase the amount of electron injection so as to improve the efficiency of electron injection.

The band gap of ZnO/ZnS heterogeneous could be changed by tuning the thickness of ZnS.\textsuperscript{110} And
Torabi et al. greatly reduced the band gap of heterostructures by adjusting the number of ZnO and ZnS layers, which provides a certain reference value for the research in the field of solar cells.\textsuperscript{111} Compared with the ordinary core-shell heterojunction structure, the 3D nanoarray structure can capture and rescatter the incident photons to enhance the light absorption, and the branching structure is more conducive to the

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4}
\caption{Three kinds of ZnO NRs patterns: (A,D) nanoflowers; (B,E) multidomain columns; (C,F) single crystal columns. Reproduced from Kim et al.\textsuperscript{107} with permission. Copyright @2012, American Chemical Society}
\end{figure}

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure5}
\caption{(A) Schematic growth process and (B–D) SEM images of ZnO arrays. Reproduced from Cheng et al.\textsuperscript{108} with permission. Copyright @2008, American Chemical Society}
\end{figure}
rapid transport of charge carriers and can enhance the charge separation and collection. Hassan et al. prepared three-dimensional (3D) hierarchical ZnO/ZnS heterojunction branching nanostructures on silicon substrates by MOCVD. The enhancement of light absorption benefited from the heterojunction branching surface, and the transition of ZnO/ZnS interface in the structure is conducive to the efficient transport and photoelectric conversion. ZnO/Si NRs arrays were coated with Ag NPs via a simple current displacement reaction and the 3D layered nanoarray structure was obtained (Figure 6).

Surface plasmon resonance effect can be used to enhance the photovoltaic performance of solar cells. Wu et al. grew ZnO NRs arrays directly on zinc foil by hydrothermal method, and then deposited Au NPs onto the tips of ZnO NRs through photodeposition reduction method, and adjusted the number of modified Au NPs by changing the reaction time, thus forming a match-like ZnO/Au heterostructure (Figure 7A–G). The plasma effect of Au NPs at the tip greatly promoted light collection and accelerated charge transform. This simple and controllable method of in situ growth of semiconductor/metal heterostructure plays an important guiding role in improving PCE of solar cells.

In addition to increasing the light absorption in the active layer of solar cells through near-field plasma enhancement or light scattering, decorating ZnO with Au NPs can also passivate the defects of ZnO. To explore the potential mechanism and electronic interaction between ZnO and Au, Olthof et al. prepared ZnO NRs by CBD. Then, Au NPs with different sizes deposited onto ZnO NRs in vacuum, the increase of energy band bending on ZnO NRs surface caused by Au was related the surface states, which was of great significance for controlling the defects of active layer.

In addition to the above methods, hydrothermal method, continuous ion layer adsorption, CBD combined with spin coating process, electric field assisted aqueous solution (EFAS) process, ion exchange, vulcanization treatment, and electrodeposition are also common methods for preparing ZnO NRs heterojunction arrays.

4 | APPLICATION OF ZnO NRs HETEROJUNCTION ARRAYS IN SOLAR CELLS

ZnO NRs arrays are selected as the main body to construct composite structures of ZnO-based heterojunction arrays, and then are used to fabricate the quantum-dot-sensitized...
FIGURE 7  (A) Schematic image of fabrication of ZnO/Au heterostructure, SEM images of ZnO (B–D) and TEM images of ZnO/Au heterostructure (E–G). Reproduced from Wu et al.114 with permission. Copyright ©2014, American Chemical Society

FIGURE 8  (A) Schematic image of structure and J–V curves (B) of QDSSC device. Reproduced from Majumder et al.120 with permission. Copyright ©2018, Elsevier
solar cells (QDSSCs) or organic–inorganic solar cells. By introducing the composite structure of NRs heterojunction array, the interface areas of heterojunction and the channel of carrier separation were increased through the strategies of energy band matching, structure design and surface modification, thus improving the efficiency of carrier separation and collection. Common heterojunctions include ZnO/CdS, ZnO/CdSe and ZnO/CdTe, ZnO/CuS, TiO₂/ZnO, and graphene/ZnO, and so on.

4.1 Quantum-dot-sensitized solar cells

To enhance the light collection ability of QDSSCs, it is possible to prepare QDSSCs by depositing different quantum dots (QDs) (CdS, CdSe, CdTe, etc.) on ZnO NRs by using the advantages of high extinction coefficient, adjustable band gap, long lifetime, high stability, and easy synthesis. Using cadmium nitrate as a precursor, Thambidurai et al. deposited CdS QDs (4 nm) on ZnO NRs (diameter: 110–200 nm) through a two-step chemical method and the efficiency of preparing CdS QDs sensitized ZnO NRs was 1.10%. As a commonly used QDs, CdSe (band gap: 1.75 eV) has a higher conduction band edge and excellent light absorption in visible light region, which makes it easier for excited electrons to be injected into ZnO.116 Pandi et al.117 sensitized CdSe QDs on ZnO NRs by continuous ion layer adsorption reaction. Because photogenerated carriers are separated only in a relatively narrow area near the interface, the solar cell with planar structure is not conducive to the
absorption of sunlight and the collection of photo-generated carriers. Therefore, the ZnO NRs array and QDs can form 3D heterojunction to solve this problem. The ZnO NRs array was grown on the seed layer prepared by zinc salt ethanol solution and used them as an N-type semiconductor layer to prepare PbS QDs cell with 3D heterojunction structure, compared with the solar cell with planar heterojunction structure, the short-circuit current density ($J_{SC}$) increased by about 40%.\textsuperscript{118} Nano-sized graphene QDs have the common characteristics of graphene and QDs, which provides more possibilities for quantum dot-sensitized batteries. Yang et al.\textsuperscript{119} prepared graphene QDs modified ZnO NRs arrays on interfinger gold electrode substrate by CBD combined with spin coating process. Under ultraviolet irradiation, the photocurrent was significantly elevated, which provided the possibility for further development of sensitized batteries using graphene QDs. Majumder et al.\textsuperscript{120} grew tapered ZnO NRs arrays on FTO substrates by hydrothermal method, compared the photoelectrochemistry of NRs and nanotapers grown under various conditions. Compared with ZnO NRs, The photoanode based on the nanotapers exhibits excellent light conversion ability (Figure 8A). Further sensitized by nitrogen-doped graphene QDs, the PEC activity of ZnO nanotapers was further improved, and the maximum light conversion efficiency reached ~1.15% (Figure 8B). In this study, the photoanodes of ZnO nanoarrays modified with nitrogen-doped graphene QDs expand the potential applications in low-cost QDSSCs.
In addition, another strategy to improve the low PCE of ZnO-based sensitized cells can introduce a protective layer on ZnO to construct a heterostructure II-type energy band matching structure. Luo et al.\textsuperscript{121} used Al-doped ZnO (AZO) glass as ZnO seed crystals and substrates to grow vertically aligned ZnO NRs through a CBD method. Then, ZnO NRs were used as templates to grow ZnO/ZnTe heterostructures in situ by wet chemical method. The optimal PCE of solar cell was 1.9%, and internal quantum efficiency was close to 100%. Rouhi et al.\textsuperscript{122} synthesized vertical-arranged ZnO/ZnS arrays with a longer carrier lifetime, higher surface area and specific volume, and more prominent light capture effect. The PCE of solar cells was ~4.07%.

To boost the light utilization, it is also a common strategy to develop the morphology and structure design of new nanoarray photoanode materials. Feng et al.\textsuperscript{123} synthesized vertically layered TiO\textsubscript{2}/ZnO arrays by a two-step hydrothermal approach (Figure 9). The PCE of TiO\textsubscript{2} nanowire/ZnO NRs QDs-based solar cells reached 3.20%. Combined with Cu\textsubscript{2}S counter electrode deposited by chemical bath, the PCE of CdS/CdSe cosensitized QDSSCs could be further optimized to as high as 4.57%.

Zhao et al.\textsuperscript{124} constructed a highly efficiency QDSSCs based on a photoelectrode of TiO\textsubscript{2}/ZnO NRs array modified with Ag NPs. The introduction of Ag NPs not only improved the light collection efficiency, promoted the dissociation of excitons, but also reduced the surface charge recombination and prolonged the electron lifetime. Therefore, the related fermi level was considered to stimulate a more negative

\textbf{FIGURE 13} Schematic diagram (A) and energy level diagram (B) of solar cell based on ZnO@TiO\textsubscript{2} core-shell arrays. Reproduced from Zhong et al.\textsuperscript{129} with permission. Copyright @2019, Elsevier

\textbf{FIGURE 14} Schematic diagram of the preparation of vertically arranged ZnO-NRs@ZnS. Reproduced from Chen et al.\textsuperscript{135} with permission. Copyright @2021, Elsevier
potential upward shift, leading to an increase in the PCE (5.92%) of solar cell containing Ag NPs modified TiO2/ZnO nanosheets photoelectrode, which was ~22% (4.80%) higher than that of solar cells without Ag nanosheets.

4.2 | Organic–inorganic solar cells

ZnO was widely used in organic–inorganic solar cells due to its excellent light transmittance, electron mobility, low cost, and low-temperature preparation. ZnO NRs arrays can provide direct electron transport channels and avoid recombination at grain boundaries, thus improving the collection efficiency of carriers. Liu et al.125 prepared uniform CuS shells surrounding ZnO NRs by consequent ion exchange (Figure 10A), and the PCE of solar cell was up to 1.02% (Figure 10B).

Rakshit et al.126 modified the heterostructure of ZnO NRs with CdS by combining hydrothermal method with pulsed laser deposition (Figure 11A–C, and solar cells were prepared with poly (3-hexylthiophene) (P3HT), CdS modified and unmodified ZnO NRs as active layers, respectively. The PCE of the corresponding solar cell after the modification of ZnO NRs by CdS was elevated by 300% than that of ZnO:P3HT solar cell, thanks to the cascade energy band structure beneficial to charge transfer (Figure 11D).

In recent years, perovskite solar cells (PSCs) based on 1D ZnO NRs still have the problem of efficiency loss. On the one hand, this problem is caused by the non-optimized morphology of ZnO NRs, and on the other hand, it is caused by defects in the active layer or at the interface of ZnO/perovskite, which will cause the recombination of charge carriers. Therefore, the key to reduce the efficiency loss is to optimize the morphology of ZnO NRs, passivate the interface defects and improve the electron transport. Commandeur et al.127 constructed a 3D all-inorganic PSCs (Figure 12). The back electrode was constructed with stripped multilayer graphite, which realized effective hole extraction. In addition, yttrium doping improves the conductivity of ZnO, thus improving the electron transport and increasing the PCE of solar cells by three times. To passivate the surface and reduce charge recombination, nano-scale TiO2 coating modification has the most significant modification on ZnO, which leads to a great improvement in charge transfer. This strategy has increased the PCE of solar cells by a total of nine times. More importantly, all-inorganic solar cells showed excellent stability, and the initial performance did not decrease after being stored for 1000 h under environmental conditions.

In the preparation of PSCs, it is necessary to consider both PCE and stability. The selection of the electron transport layer should systematically consider factors, such as light absorption performance, interface smoothness, electron transport performance and preparation technology process. PSCs usually adopt TiO2 as a photoanode, but the low electron mobility of TiO2 may lead to unbalanced charge transport in PSCs.128 Zhong et al.129 prepared Glass/FTO/ZnO/ZnO@TiO2/CH3NH3PBI3/Spiro-OMeTAD/Au solar cells using ZnO@TiO2 core-shell structure as electron transport layer (Figure 13A). Based on the matching of the energy level of ZnO@TiO2 electron transport layer and perovskite (Figure 13B), it is conducive to effective electron injection from CH3NH3PBI3 to TiO2 and then from TiO2 to ZnO. Compared with ZnO-based solar cell, the performance of solar cells based on ZnO@TiO2 nanosstructure has been improved. The modification of TiO2 leads to the increase of open circuit voltage (VOC) and fill

| TABLE 1 Performance of solar cells based on different structures |
|---------------------------------------------------------------|
| Structures | V<sub>OC</sub> (V) | J<sub>SC</sub> (mA·cm<sup>−2</sup>) | FF | PCE (%) | References |
|CdSe QDs sensitized ZnO NRs | 0.41 | 13.7 | 0.37 | 2.1 | 117 |
|ZnO/ZnTe | 0.583 | 7.26 | 0.45 | 1.90 | 121 |
|ZnO–ZnS | 0.68 | 12.2 | 0.49 | 4.07 | 122 |
|TiO2/ZnO-CuS | 0.512 | 16.11 | 0.55 | 4.57 | 123 |
|TiO2/Ag/ZnO/CdS/CdSe QDs | 0.704–0.744 | 13.27–15.65 | 0.514–0.508 | 5.92 | 124 |
|ZnO/CuS/P3HT | 0.391 | 4.9 | 0.53 | 1.02 | 125 |
|CdS-decorated ZnO NRs:P3HT | 0.557 | 1.674 | 0.40 | 0.38 | 126 |
|ZnO/TiO<sub>2</sub> NRs | 0.910 | 19.94 | 0.56 | 10.24 | 129 |
|ZnO/Cu<sub>2</sub>O | 0.557 | 11.42 | 0.498 | 3.17 | 130 |
|ZnO Nano-Ripple with ALD-ZnO | 0.672 | 17.9 | 0.659 | 7.96 | 132 |
|ZnO/ZnS/perovskite | 1.10 | 23.48 | 0.71 | 16.2 | 135 |
factor (FF), and the improvement of stability. More CH3NH3PbI3 perovskite in NRs and less PbI2 residue in perovskite film, which is committed to the improvement of JSC. The maximum PCE of solar cell reached 10.24% at the relative humidity of 40%.

In addition, the stability and repeatability of PSCs are also important factors that restrict its development. Although ZnO has high electron mobility, ZnO NRs arrays have the ability to increase light absorption and provide direct electron extraction channels, making them ideal materials for electron transport layers.130-132 However, due to the poor chemical compatibility between ZnO and perovskite layer, the stability based on ZnO is relatively poor.133,134 Zhang et al.135 sulfurized ZnO NRs at about 400 nm and obtained the corresponding ZnO/ZnS heterojunction structure (Figure 14), which promoted the transfer of charge carriers to a certain extent, and the PCE was improved to 11.72% when it was applied to perovskite solar cells.

Overall, the efficiency of solar cells based on ZnO NRs heterojunctions is still low (Table 1), to further improve the efficiency and stability of solar cells, it will be a hot research direction in the future to find low-cost and high-stability ZnO NRs heterojunction array as a light absorption layer, match the corresponding hole transport layer, further simplify the solar cell structure and improve the packaging process. Exploring the photoelectric properties and transport mechanism of ZnO-based NRs heterojunction array structure will contribute to the design of more efficient solar cell materials.

5 CONCLUSIONS AND PROSPECT

ZnO NRs has attracted much attention in optoelectronic devices due to its unique semiconductor characteristics, especially its excellent exciton binding energy, high electron mobility, and high surface area, which are conducive to light collection and has become the main material for constructing solar cells. ZnO NRs are often used as photoanode or active layer of solar cells, but simple ZnO NRs materials can no longer meet the demand for high photoelectric conversion rate. In this paper, we reviewed the recent research on the construction of ZnO NRs heterojunction, improving the light capture ability of NRs and prolong the electron lifetime. CVD, electrochemical deposition, hydrothermal method, and their combined technologies were introduced to construct the heterojunction array of ZnO NRs with controllable structure, which were applied to the preliminary work of different types of solar cells. Although many excellent works have been done in solar cells based on ZnO heterojunction arrays, there are still some limiting factors in the development of solar cells, such as low PCE, short lifetime of solar cells, material instability, high cost and toxicity of materials. Therefore, the future work should focus on optimizing the material growth, structure design, electrode contact and light capture efficiency of solar cells to improve the excellent performance of solar cells. In addition, the growth mechanism of ZnO NRs heterojunction array in the growth process needs to be further studied. Combined with machine learning, the heterojunction materials matching with ZnO NRs are screened, and experimental conditions should be optimized to realize controllable preparation of ZnO NRs heterojunction array in terms of density, size, aspect ratio and growth orientation. With the help of DFT theoretical calculation method, the transport mechanism of heterojunction interface carriers is theoretically provided. By regulating the aspect ratio of NRs, the transport performance of interface carriers can be effectively expanded and improved, and the dissociation probability of excitons can be improved, so as to further improve the photoelectric performance of solar cells, which will also be the future development direction.

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CONFLICT OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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