One-dimensional coaxial nanowire solar cell

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Abstract: Solar cell is a promising candidate for clean and renewable energy power. But high cost and low energy conversion efficiency are bottlenecks for its applications. In recent years, big progresses have been made in developing solar cells with reduced cost and increased efficiency. In this paper, we review recent studies on a new type of solar cells based on coaxial nanowires (NWs) and their arrays. The advantages and the photovoltaic properties of this kind of solar cells will be depicted first. Then the methods for improving efficiency will be discussed. Finally, some innovative designs of the solar cell structures and the potential applications of such solar cells will be summarised.

Keywords: solar cell; clean energy; coaxial nanowire; nanowire array.

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1 Introduction

With the energy shortage and environmental pollution becoming more and more serious, searching for renewable clean energy source and energy conversion techniques are very important for social development. Solar energy is one of the most abundant natural energy sources and solar cells can convert solar energy into electricity directly, so solar energy and solar cells are the most promising candidates. Tremendous researches are attracted in this area.

Since the first practical semiconductor solar cell with an efficiency of 6.0% was fabricated in Bell Labs in 1954, it has been half a century. Today, the dominative solar cells on the market are single-crystalline and polycrystalline silicon (Si) solar panels which convert sunlight into electricity at efficiencies around 20%. To maintain or increase the efficiency, expensive processing and refining are required, which increase the cost, and thus limit the large-scale production and application of Si solar cells. Second, generation solar cells were based on thinner semiconductor films, such as CdTe and amorphous Si (Ginley et al., 2008; Shah et al., 1999). These solar cells reduced the cost at the expense of their efficiency. In addition, excitonic solar cells, such as polymer-inorganic hybrid cells and dye-sensitised solar cells (DSSCs) also attracted intense studies (Kannan et al., 2003; Huynh et al., 2002; Oregan and Gratzel, 1991). However, these solar cells often need rare or expensive methods and/or materials, and can only be constructed in laboratory-scale.

Recent theoretical studies indicated that coaxial nanowire (NW) structures could improve carriers' collection and overall efficiency compared with single-crystal bulk semiconductors of the same materials (Kayes, et al., 2005; Zhang et al., 2007). They are potential new generation of solar cells with large-scale, high-efficiency and low-cost. Therefore, one-dimensional coaxial NW solar cells are currently in active research (Hochbaum and Yang, 2010).

In this paper, we review the advantages and the photovoltaic properties of the solar cells based on coaxial NWs and their arrays, discuss methods for improving efficiency and describe some innovative designs of the solar cell structures and the potential applications of the solar cells.

2 Advantages of the coaxial NW solar cells

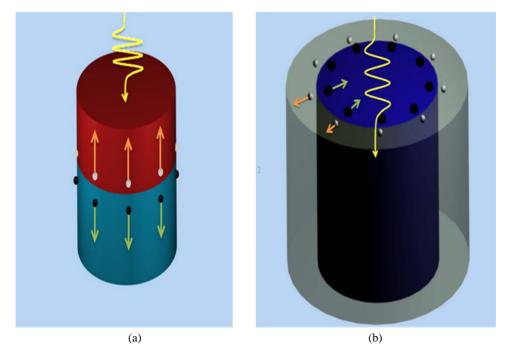
Compared with conventional planar solar cells, solar cells based on coaxial semiconductor NWs and their arrays have the following advantages, which are vital for producing high-efficiency, low-cost and easy-integration solar cells.

2.1 Enhanced conversion efficiency.

Solar cells depend on the optical absorption and separation of electron-hole pairs under the built-in field established across the p-n junction. That is to say, the energy conversion efficiency is determined by the absorption efficiency of the material and the lifetime of minority carrier.

To increase the conversion efficiency, it is necessary to avoid the bulk recombination of the carriers and ensure the carriers reach the depletion region. Therefore, the conventional planar solar cell shown in Figure 1(a) should possess high quality and be thin enough (Kayes et al., 2005). But the thin planar solar cell is disadvantageous to the optical absorption. The contradiction hinders increasing the efficiency of the solar cells.

Figure 1 Schematics of two kinds of solar cells. (a) Conventional planar solar cells. The upper section is a p-type semiconductor; the lower section is a n-type semiconductor. Light is incident through the upper surface, and the light-generated carriers are extracted vertically near the interface; (b) One-dimensional coaxial NW solar cells. The core is a p-type semiconductor; the shell is a n-type semiconductor. Light is incident along the axis, and the light-generated carriers are extracted laterally near the interface. (see online version for colours)



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In the coaxial NW with radial p-n junction, p-n interface extends along the axial direction of the NW as shown in Figure 1(b) (Kayes et al., 2005). Carriers' separations take place in the radial direction instead of the axial direction. The carriers' collection distance is comparable to the minority carrier diffusion length or even smaller. Hence, photon generated carriers can reach the p-n junction efficiently without substantial bulk recombination. By orthogonalising the direction of light absorption and carriers' separation, the wire with optimised size provides not only an effective absorption of the photons, but also efficient carriers' separation and collection. As a consequence, the efficiency could be enhanced remarkably.

Actually, theoretical studies have shown that coaxial NWs with radial p-n junctions could improve carriers' collection and overall efficiency compared with single-crystal bulk semiconductors. Taking Si NW-based solar cells as an example, the efficiency can achieve 15% to 18% depending on the configuration and the NW quality (Kayes et al., 2005).

2.2 Lower cost

As a consequence of the radial collection mechanism, the materials' quantity and quality can be lower than traditional p-n junction devices without causing considerable bulk recombination. Thus the coaxial solar cells can greatly reduce the cost and maintain high conversion efficiency at the same time. It was reported that the Si NWs array which have less than 5% a real fraction of wires can gain up to 96% peaking absorption and they can absorb up to 85% of day-integrated above-band gap direct sunlight. In addition they have enhanced near-infrared absorption. And they show an external quantum efficiency of 0.85 due to a radial junction near the interface. So the enhanced optical absorption and carriers' collection can enable a solar cell just use one percent of the material for traditional wafer based PV devices, but gain increased PV efficiency owing to an enhanced absorption (Kelzenberg et al., 2010).

2.3 Reduced reflectance of light

Oriented NW arrays have been shown to possess reduced surface reflectance which is significant to improve energy conversion efficiency of solar cells. For example, Mg-doped GaN NWs grown on Si substrates have an average reflectance of 10.1% and a conversion efficiency of 2.73% (Tang et al., 2008). Si NW based solar cells on glass substrates fabricated by wet electroless chemical etching exhibit low reflectance (<10% at 300–800 nm) and a strong broadband optical absorption (>90% at 500 nm). According to the highest open-circuit voltage and short-circuit current density at AM1.5 illumination, the maximum power conversion efficiency were calculated to be 4.4% (Sivakov et al., 2009).

2.4 Well-developed coaxial NWs and NW array preparation methods

Many methods have been developed for the fabrication of NWs and NW arrays, such as template-based method, catalyst-guided growth, electrospinning technique, electron-beam lithography (EBL) and so on. These techniques can precisely and easily control nanomaterials' parameters, including chemical/dopant composition, diode junction structure, size, and morphology. These parameters are crucial for PV performance.

2.5 Easier integration

Through microfabrication and micromanipulation, integration of multiple NWs or cells in series and in parallel can be carried out to output higher energy and to drive larger loads (Tian et al., 2007; Xu et al., 2010).

3 Coaxial NW solar cells

3.1 Coaxial Si NW solar cells

In the past decades, a large variety of technologies have been developed to produce commercial Si solar cells. In addition, with the development of the semiconductor industry, the synthesis and integration of Si NWs with controlled doping, morphology, and contacts can be realised easily. Therefore, Si is a good choice for systematic investigation of the influences of NW structures on solar energy harvesting. The single coaxial Si NW solar cells were fabricated in laboratory for the first time in 2007 (Tian et al., 2007), though the theoretical studies were several years earlier (Kayes et al., 2005). Si NWs with p-n and p-i-n radial junctions were synthesised by VLS growth mechanism and subsequent deposition of thin film (Tian et al., 2007). After multiple EBL steps, carefully Si etching and contacting p- and n-type regions separately, the single NW solar cells were fabricated. But, such solar cells showed very low conversion efficiency. After the insertion of an intrinsic silicon thin-film layer between the p-type and n-type layers, the single NW solar cells showed a still low open circuit voltage (V_{oc}) of 0.26 V but an extraordinarily high short-circuit current density (J_{sc}) , which was attributed to strongly enhanced absorption in the thin-film shell because of its nanocrystalline nature. Ultimately, an overall efficiency of 2.3%-3.4% was obtained.

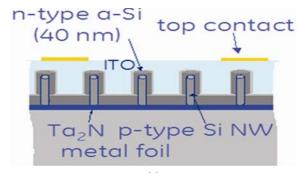
After the first realisation of the single Si coaxial NW solar cells, a lot of works have been focused on solar cells based on coaxial NW arrays with radial p-n junctions.

Wafer-scale Si NWs array with radial p-n junctions was synthesised by low-temperature etching and thin film deposition method in Yang's group (Garnett and Yang, 2008). The solar cells exhibit cell efficiencies of about 0.5%. The low efficiency can be attributed to two reasons. One is the interfacial recombination loss which is evidenced by a significant dark current; another is a large series resistance (R_s) of the polycrystalline shell.

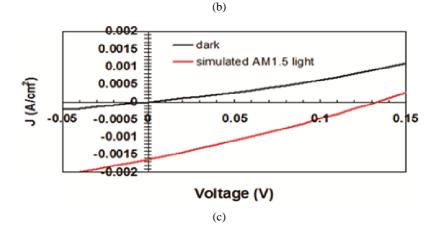
In another group, by coating a PECVD conformal n-type amorphous silicon layer on p-type Si NW array to form p-n junctions, a new kind of solar cell was fabricated (Figure 2). This solar cell gains an even lower efficiency of 0.1% which results from the large contact resistance and low shunt resistance (R_{SH}) (Tsakalakos et al., 2007).

For solar cells based on coaxial NWs, their efficiencies obtained in experiments are far less than the theoretical calculations and cannot satisfy the application requirements (Kayes et al., 2005). So, how to increase the efficiency of the coaxial NW solar cell while lowering its cost is a huge challenge.

The power conversion efficiency of a solar cell is defined as: $\eta = (FF \times J_{SC} \times V_{OC}) / P_{in}$, where *FF* is the fill factor, and P_{in} is the incident light power density. So power conversion efficiency can be enhanced by increasing the open circuit voltage, fill factor or short circuit current density. For this purpose, simple methods for making solar cells from arrays of silicon NWs with radial p-n junctions were developed, and surface roughness, NW's diameter and density were precisely controlled. Figure 2 Structure and optoelectronic characteristics of the demonstrated all-inorganic silicon NW solar cell. (a) Schematic cross-sectional view of the Si NW solar cell architecture. The NW array is coated with a conformal a-Si: H thin film layer; (b) Scanning electron micrograph (plan view) of a typical Si NW solar on stainless steel foil, including a-Si and ITO layers with insets showing a cross-sectional view of the device and a higher magnification of an individual Si NW coated with a-Si and ITO; (c) Dark and light (under simulated AM1.5 conditions) current-voltage characteristics of a typical Si NW solar cell. (see online version for colours)

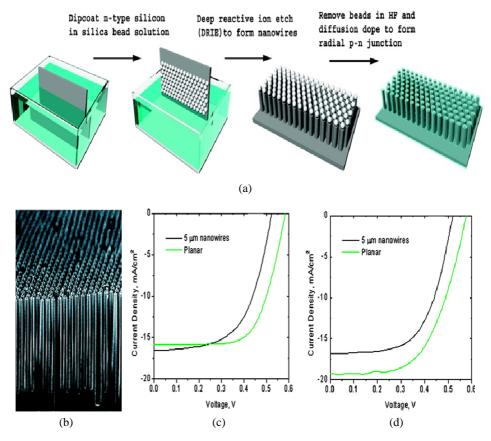


(a) 8 μm



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Figure 3 (a) Ordered silicon NW array fabrication scheme (b) tilted cross-sectional SEM of a completed ordered silicon NW radial p-n junction array solar cell made by bead assembly and deep reactive ion etching (c) solar cell output characteristics of 5 μm NW and planar control solar cells fabricated from an 8 μm thin silicon absorber (d) solar cell output characteristics of the same structures as in panel c, but using a 20 μm thin silicon absorber (see online version for colours)



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An interesting method was demonstrated to fabricate large-area Si NW radial p-n junction PV devices by taking three steps (Garnett and Yang, 2010): dip coating a Si substrate to self-assemble silica spheres on it, deep reactive ion etching (DIRE) to form NWs, and diffusion to form the p-n junction. The detailed procedures are demonstrated in Figure 3. Highly doped n-type Si wafers with a thin, lightly doped epitaxial layer (8 and 20 μ m thick) on top were used as substrates. NW arrays were formed by partial etching of the epitaxial layer. The achieved conversion efficiencies are 4.8% and 5.3% for these 8 and 20 μ m silicon absorber layer, separately. The morphology of NW makes solar cell exhibits not only extraordinary light trapping but also dramatically increased surface area and junction recombination property. The improved light absorption and increased surface recombination compete against each other. For very thin absorbing layers the light-trapping effects dominate, while for thicker cells which show outstanding

optical absorption, the recombination effect is predominant. This simple fabrication process for solar cell based on ordered vertical NW array represents a feasible path toward high-efficiency, low-cost coaxial NW array solar cells. Further optimisation could lead to cells with efficiencies close to bulk silicon.

3.2 Other semiconductor coaxial NW solar cells

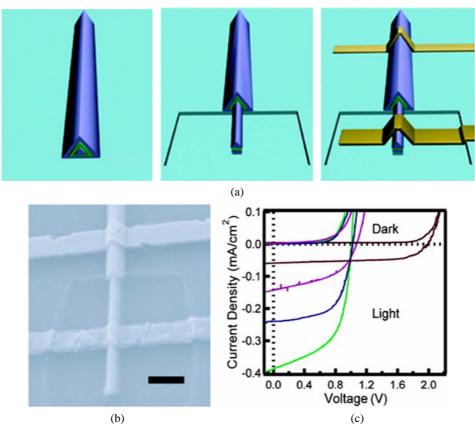
Most previous researches of NW solar cells have focused on Si NWs whose doping and morphology can be readily controlled. But Si is not the best material for solar cells because it is an indirect band gap semiconductor. For indirect band gap semiconductor, a photon must be absorbed or emitted during the electron transition to keep the total momentum constant, which limits light absorption in nanoscale semiconductor. Therefore, finding new semiconductors with direct band gap and good solar spectral absorption is necessary to increase the optical absorption and the efficiency of the solar cells.

Extensive researches have been attracted to solar cells made from III–V materials because III–V materials are direct band gap semiconductors. At the same time, by changing the alloy composition, their band gap can be tuned to span nearly the entire solar spectrum from 0.7 to 3.4 eV. These two characters of III–V materials make more than 85% of the incident light with energy above the band gap can be absorbed within a thickness of several hundreds nanometres. However, nearly all of these devices were thin-film cells (Jani et al., 2007; Neufeld et al., 2008; Kozodoy et al., 1998). III–V coaxial photovoltaic devices remain to be studied (Dong et al., 2009; Czaban et al., 2009; Wei et al., 2009).

Lieber's group reported the first experimental realisation of coaxial group III-nitride NW photovoltaic devices, n-GaN/i-In_xGa_{1-x}N/p-GaN, by metal-organic chemical vapour deposition (MOCVD) (Figure 4) (Dong et al., 2009). By adjusting indium mole fraction, the active layer band gap and hence light absorption can be tuned, which was further confirmed by the electroluminescence measurements. A single NW solar cell was fabricated by selective etching and contacting the p-type and n-type regions separately. Simulated one-sun AM 1.5G illumination yielded open-circuit voltages from 1.0 to 2.0 V and short-circuit current densities from 0.39 to 0.059 mA/cm² as the indium composition is decreased from 0.27 to 0. A maximum efficiency is about 0.19%. This kind of NW solar cell exhibits excellent robustness and enhanced efficiencies for concentrated solar light illuminations. Single NW J_{sc} values as high as 390 A/cm² could be obtained under intense short-wavelength illumination. By improving the crystal quality of the In-rich InGaN layer, the photovoltaic properties of the coaxial III-nitride NW solar cells will be improved.

Cd(S, Se, Te) is another potential candidate for solar cell because it has been reported that nanopillar arrays of this material exhibit enhanced collection of low-energy photons absorbed far below the surface, as compared with planar photoelectrodes (Spurgeon et al., 2008). A PV structure that was composed of highly oriented, three-dimensional (3D), single-crystalline n-CdS nanopillars, embedded in polycrystalline thin films of p-CdTe (Figures 1 and 2 in Fan et al., 2009) was demonstrated by Javey's group. The n-CdS nanopillar arrays were prepared by the template-assisted VLS growth method. This method simplified the fabrication process of PV devices based on crystalline compound semiconductors with controlled density, optimised size and high orientation.

Figure 4 (a) Schematics of device fabrication: left, coaxial n-GaN/i-In_xGa_{1-x}N/p-GaN NW heterostructures; middle, exposed the n-core at NW end following ICP-RIE etch; right, Ni/Au and Ti/Al/Ti/Au metal contacts deposited on the p-shell and n-core, respectively; (b) SEM image of a representative NW device. Scale bar is 2 μm; (c) Dark and light *I*-V curves of representative ultraviolet, purple, blue, and green NW PV devices. The ultraviolet, purple, blue, and green denote cells with In compositions (x) of 0, 5.6%, 14.9%, 27%, respectively and decreasing band gap of In_xGa_{1-x}N layer. (see online version for colours)



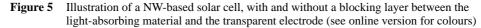
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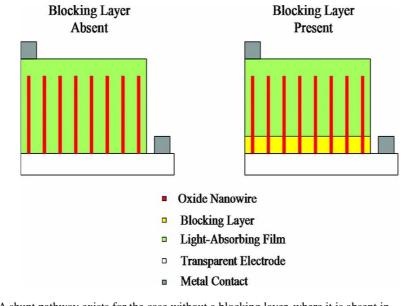
From the I-V curves of a typical cell at different illumination intensities shown in Figure 3 in Fan et al. (2009), an efficiency of 6% is obtained which is higher than most of the previously reported PV device based on nanostructured materials. Through improving top contacts with higher optical transparency and lower parasitic resistances, the enhanced efficiency is expected to be obtained in the future.

To confirm the effects of the geometric configuration of the nanopillars on the overall conversion efficiency, experiments and theoretical simulations were carried out. As revealed by Figure 4 in Fan et al. (2009), the space charge and carrier collection region is enhanced with the increasing embedded nanopillar height, which reduces the total volumetric recombination of photo-generated carriers. However, the interface recombination cannot be ignored in such cells, which was the key limiting factor for the performance of solar cells.

By embedding the 3D solar nanopillar cell in polydimethylsiloxane (PDMS), a mechanically flexible solar cell was fabricated. Experiments and modeling show that the bending of the devices affect the cell performance only at the edge of the device, and the cell is highly robust and stable under repetitive bending. The mechanically flexible solar cell is of particular interest for a number of practical applications.

In addition, p-type cuprous oxide (Cu₂O) is also one of the most widely studied inorganic materials as a substitute material for Si, because it allows for good solar spectral absorption. An all-oxide solar cell consisting of vertically oriented n-type zinc oxide (ZnO) NWs surrounded by a film constructed from p-type Cu₂O nanoparticles was fabricated by a simple solution-based approach (Yuhas and Yang, 2009), as shown in Figure 5. After the insertion of a blocking layer of TiO₂ between the NWs and the film, the efficiency of the cell can reach 0.05% which was 50 times larger than the cell without it. Increase of the $R_{\rm SH}$ is an effective manner to enhance the performance of the solar cell.





Note: A shunt pathway exists for the case without a blocking layer, where it is absent in the case with the blocking layer.

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4 Methods to increase the output characteristics of the one-dimensional coaxial NW solar cell

As mentioned above, the efficiency of the one-dimensional coaxial NW solar cell is primarily affected by surface or interface recombination and inner resistance.

The surface or interface is located directly at the p-n junction in the one-dimensional coaxial NW solar cell. For the NWs and their arrays, the high surface to volume ratio is

one of the most important peculiarities. Severe surface/interface recombination can be dominant in the devices. Therefore, the solar cells' efficiency is significantly improved by reducing the recombination processes, for example, by improving the crystalline quality of the shells and/or passivating the NW surface (Aberle, 2000).

In any solar cells, the parasitic resistances can be divided into the $R_{\rm S}$ and the $R_{\rm SH}$. Both of them lead to the loss of photovoltaic efficiency. The $R_{\rm S}$ includes components such as inherent resistance of the semiconductors, as well as metal-semiconductor contact resistance. And the $R_{\rm SH}$ includes the resistance of alternate electrical pathways that do not contribute to the photocurrent. In an ideal solar cell, $R_{\rm S}$ is zero, and $R_{\rm SH}$ is infinite. It has been reported that a single NW coaxial p-n junction solar cell with the smaller $R_{\rm S}$ of the shell possesses the higher $J_{\rm sc}$ and efficiency (Tian et al., 2007), when compared with the radial p-n junctions on NW arrays synthesised by low-temperature wafer-scale etching and thin film deposition method (Garnett and Yang, 2008). For the all-oxide solar cell fabricated from vertically oriented ZnO NWs and Cu₂O nanoparticles, the role of the TiO₂ blocking layer on the ZnO NW array is to sufficiently increase $R_{\rm SH}$ such that the efficiency of the solar cell rises by a factor of 50 compared with the cell without the TiO₂ blocking layer (Yuhas and Yang, 2009). It can be concluded that reducing the $R_{\rm S}$ and increasing the $R_{\rm SH}$ can enhance the efficiency of solar cell remarkably.

Except for the two intrinsic factors mentioned above, integration of multiple NWs in series or in parallel can scale the output characteristics and thus drive large loads. For example, the coaxial silicon NW solar cells were interconnected in series and in parallel (Tian et al., 2007). I-V data show that interconnection of the two elements in series and parallel yields V_{oc} and I_{sc} values, respectively, that are approximately the sum of two, as expected (Tian et al., 2007).

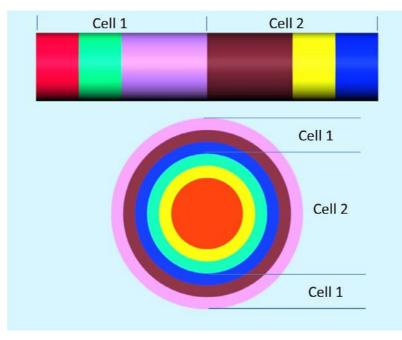
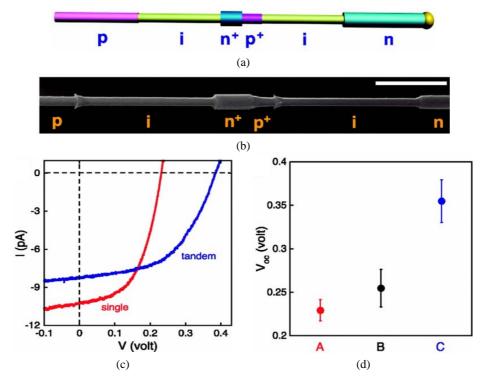


Figure 6 Schematics of axial and coaxial NW tandem solar cells (see online version for colours)

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Traditional planar tandem-cells (Ginley et al., 2008; Dimroth and Kurtz, 2007; King et al., 2007) contain different semiconductors stacked in descending order of band-gap to assist in light harvesting. They show high energy conversion efficiency far beyond 31%, but the higher cost hinders their development. During the synthesis of NW, by integrating multiple p-i-n diodes or cells through axial or radial extension on a single NW, tandem devices with appropriate modulation of dopant concentration can be readily created in semiconductor NW heterostructures (shown schematically in Figure 6), and the voltage and output power can be scaled (Tian et al., 2009; Kempa et al., 2008). A single Si-NW tandem solar cell with a p-i-n⁺-p⁺-i-n (i = 2 μ m) axial modulation has been prepared (Figure 7) (Kempa et al., 2008). The mean V_{oc} for p-i-n⁺-p⁺-i-n tandem solar cell is larger than that of the single p-i-n device. In particular, the mean $V_{\rm oc}$ has increased 57% over the value for p-i-n (i = 2 μ m) and 39% over p-i-n (i = 4 μ m) devices. The power output of the tandem solar cell is 3.2 pW, 39% larger than that of the equivalent single p-i-n device. Parasitic $R_{\rm S}$ at the n⁺/p⁺ interface leads to that the increase in $V_{\rm oc}$ and output power are smaller than ideal case. The successful preparation of the single Si NWs tandem solar cell with a p-i-n⁺-p⁺-i-n axial modulation denotes the possibility of radial tandem devices.

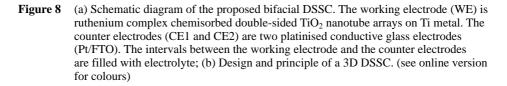
Figure 7 Tandem axial Si NW photovoltaic devices. (a) Schematic of two p-i-n diodes integrated in series on a single NW; (b) SEM images of a selectively etched tandem p-i-n⁺-p⁺-i-n SiNW; scale bar is 1 μ m; (c) *I*-*V* responses recorded on p-i (2 μ m) -n (red) and p-i-n⁺-p⁺-i-n, i = 2 μ m (blue) SiNW devices under AM 1.5G illumination; (d) V_{oc} for p-i (2 μ m) -n (red), p-i (4 μ m) -n (black), and p-i-n⁺-p⁺-i-n, i = 2 μ m (blue) axial SiNW devices. Error bars are ±1 standard deviation. (see online version for colours)

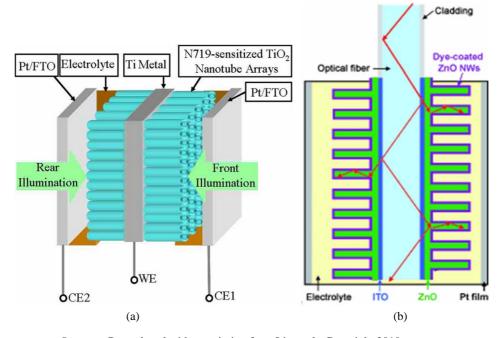


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To enhance the optical absorption and subsequently the output characteristic, other innovative designs of the solar cell structures are invented.

For conventional silicon solar cells, a bifacial configuration (Hübner et al., 1997; Hezel, 2003) is advantageous because it has two carrier-collecting p-n junctions. Nearly twice greater output power was achieved when using bifacial silicon solar cells to collect the Albedo radiation from the environment (Cuevas et al., 1980). At present, a bifacial DSSC has been fabricated as shown in Figure 8(a) (Ito et al., 2008; Liu and Misra, 2010). The bifacial DSSC under double-sided illumination is substantially equivalent to two parallel monofacial DSSCs. More output power can be generated by the bifacial DSSCs by collecting more radiation, although the overall conversion efficiency remains unchanged.





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An innovative 3D DSSC [Figure 8(b)] attracts extensive attention recently (Weintraub et al., 2009). The hybrid structure of 3D DSSC contains ZnO NWs growing normal to the optical fibre surface which enhances the surface area for the interaction of light with dye molecules. The light illuminates the fibre from one end along the axial direction, and its multiple reflections within the fibre increase the light travel distance and the opportunities for energy conversion at the interfaces. When compared with the case of

light illumination normal to the fibre axis from outside the device, the efficiency of the 3D DSSC is enhanced by a factor of up to six. Furthermore, the full-sun energy conversion efficiency (AM 1.5 illumination, 100 mWcm⁻²) can reach 3.3%, which far surpasses the highest value reported for ZnO NWs grown on a flat substrate surface and that of ZnO NWs coated with a TiO₂ film.

The design concepts are applicable to one-dimensional coaxial NW solar cell and represent an area for future studies.

5 Conclusions

Novel solar cells based on one-dimensional coaxial NWs and their array display promising improvements over planar solar cells. It can serve as robust power sources and provide power for nanoelectronics which consume power at the nano-watt scale, like biosensor (Tian et al., 2009) and pH sensor (Tian et al., 2007). Notably, two series interconnected Si-NW PV elements were used as the sole power supply to drive a NW-based AND logic gate (Tian et al., 2007). Such results predict that with full optimisation and improvement, one-dimensional coaxial NW solar cell can function effectively as integrated power sources for practical nanoelectronic device applications in future. To pursue this goal, further efficiency improvements must be realised.

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