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Novel solar cells in a wire format

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Photovoltaic devices in a wire format have recently attracted increasing attention as, compared with the conventional planar structure, they show unique and promising advantages. For instance, they are light-weight and can be easily woven into clothes or integrated into other structures, which enable applications in electronic textiles and various complex devices. In this tutorial review, the recent advancement in photovoltaic wires including both dye-sensitized and polymer solar cells are described.

Two main architectures based on a single core-sheath fiber and twisted fibers are carefully illustrated with an emphasis on the comparison of various substrates which have been focused in past

development. The current challenge including low energy conversion efficiency and low stability and

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Key learning points

Wire-shaped solar cells show unique and promising advantages compared with their planar counterparts. Both dye-sensitized and polymer solar cells in a wire format are described. Two main architectures with different electrodes are compared. The current challenge and future direction of wire-shaped solar cells are summarized.

future direction of the wire-shaped cell have been finally summarized.

1. Introduction

1.1. Classification and characterization of solar cells

Photovoltaic devices, also called solar cells, which convert solar energy to electric energy, represent a promising technology to use renewable energies. According to the used photoactive materials, solar cells can be divided into silicon-based (including monocrystalline, polycrystalline and amorphous silicon), semiconducting compound-based (including gallium arsenide and copper indium gallium selenide) and organic solar cells. The working principle of a silicon solar cell is based on a photovoltaic effect of a p-n junction occurring at the interface between p- and n-type semiconductors. A built-in electric field being directed from n- to p-type regions is formed at the p-n interface with a reverse drifting of the carriers to finally reach equilibrium. Electron-hole pairs are produced when the energy of incident photons at the p-n junction is higher than the band gap energy of the material. Under the built-in electric field, the electrons are transported in the n-type material while the holes are transported in the p-type material. The electrons and holes are then collected at their respective electrodes. Due to the highest efficiency, the silicon solar cell currently dominates the photovoltaic market.¹ However, a large-scale application of silicon

solar cells has been hindered by high cost and pollution during the production. Different from the silicon solar cell using the same material with different semiconductive properties, a semiconducting compound based solar cell was realized by using two types of compounds to build the p-n junction but shares the same working principle. The semiconducting compound-based solar cell is hindered by limited sources of rare metals and difficulty in synthesizing semiconducting materials with high purity. Therefore, more and more attention has recently been paid to develop nextgeneration photovoltaic devices such as dye-sensitized solar cells (DSC) and polymer solar cells (PSC) with easy solution fabrication, low cost and flexible structure.^{2–5}

The performance of a solar cell is generally characterized by current–voltage curves being obtained in the dark and under standard light illumination (AM 1.5). There is no current flow in the dark, while a photocurrent will be generated under light (Fig. 1). The power conversion efficiency (η) is determined by the equation of $\eta = V_{\rm oc}^* J_{\rm sc}^* FF/P_{\rm in}$, where $V_{\rm oc}, J_{\rm sc}$, FF and $P_{\rm in}$ correspond to the open circuit voltage, short circuit current, fill factor and incident light power density (100 mW cm⁻² for AM 1.5). The fill factor is defined by FF = $P_{\rm max}/V_{\rm oc}^* J_{\rm sc}$, where $P_{\rm max}$ is the largest power output.

1.2. Organic solar cells

DSCs were first demonstrated by Grätzel and co-workers in 1991.² Currently, a maximum efficiency of 12.3% had been

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Fig. 1 Typical current-voltage characteristics of a solar cell in the dark and under light irradiation.





achieved by designing new photosensitive dyes with a broad light adsorption range.⁴ In a typical DSC device (Fig. 2), transparent conductive glass (i.e., fluorine-doped tin oxide, FTO) coated with a layer of porous semiconductor metal oxide (e.g., titanium dioxide) is used as a photoanode while another conductive glass coated

with platinum functions as the counter electrode. A redox electrolyte typically containing I_3^{-}/I^{-} is filled into the space between two electrodes. Electrons are produced when the light is absorbed by the dye molecules, which will inject into the conduction band of metal oxide. The injected electrons diffuse in the semiconductor network and are collected at the transparent



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Fig. 3 (a) Schematic illustration of the conventional planar PSC with bulk heterojunction structure. (b) Schematic illustration of the charge transfer in a PSC.

FTO electrode, which transport to the counter electrode through the external circuit. The dye cations are reduced to the neutral state by I^- ions with production of I_3^- ions which further revert to I^- ions by accepting electrons at the counter electrode.

Different from the DSC, the PSC had been well known as excited solar cells that are typically composed of photoactive materials sandwiched by two electrodes (Fig. 3a).³ The photoactive material includes a conjugated polymer as an electron donor and a C60 derivative as acceptor, and often appears in an interpenetrating network with bulk heterojunction structure. Due to a large interface area between donor and acceptor, the bulk heterojunction structure favors separation of the generated excitons and improves transport of the free charge carriers. The photoelectric conversion process contains the following four basic steps (Fig. 3a). (1) Excitons (coulombically bound electron and hole) are produced when electrons are excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in the polymer donor upon absorption of light energy. (2) Excitons diffuse to the interface between donor and acceptor in the photoactive layer. (3) The excitons are separated into free holes and electrons under the built-in electric field. (4) Holes are transported along the conjugated polymer backbone, while electrons hop among the fullerene acceptor. The holes and electrons are collected by the respective electrodes. Recently, PSCs with a maximum efficiency of 9.2% were realized based on an inverted structure and interface modification between photoactive layer and electrode.⁵

1.3. Necessity for organic solar cells in a wire shape

For both DSC and PSC, a promising advantage lies in that they can be made in a flexible structure based on plastic conductive substrates (*e.g.*, polyethylene terephthalate film coated with indium tin oxide).^{6–8} However, for DSCs, the plastic conductive substrate with low thermal stability greatly limits their photovoltaic performance as they cannot withstand the high sintering temperature for semiconducting metal oxide (*e.g.*, 450–500 °C for titania) during the fabrication.^{7,8} Although flexible PSCs could be produced at a large scale by screen printing or roll–to–roll process, the energy conversion efficiency was relatively low (*e.g.*, less than 2%).⁶

To achieve a flexible DSC or PSC with high efficiency and high stability, the design of wire structures with various inorganic fibers as substrates may provide an effective solution.^{9–13} Currently, for both DSCs and PSCs, the wire devices can be constructed on a single fiber (Fig. 4a) by a layer-by-layer method or by twisting fiber electrodes (Fig. 4b) typically with diameters of tens to hundreds of



Fig. 4 (a) and (b) Schematic illustrations to wire-shaped solar cells based on a single fiber electrode and two twisted fiber electrodes, respectively. (c) The maximum efficiencies of DSCs and PSCs in wire and planar formats. The data were summarized from ref. 4, 5, 12–14, 16, 18, 25 and 34.

micrometers and lengths of millimeters to centimeters. Metal wires based on copper, silver, titanium and steel have been mostly explored, and the other fiber materials including polymer fibers coated with conductive layer and carbon-based fibers are also widely investigated. Wire-shaped solar cells with the highest efficiencies based on different conductive substrates have been compared in Fig. 4c. The highest efficiencies are 7.02% and 3.87% for wire-shaped DSCs and PSCs, respectively. Herein, the recent advancement of wire-shaped DSCs and PSCs mainly including the design of different architectures and development of various wire conductive substrates is first described. The challenge and future development of the wire-shaped cell are then summarized.

2. DSCs in a wire format

2.1. Core-sheath architecture based on a single fiber

Learning from the conventional planar structure, wire-shaped DSCs had been originally fabricated by coating photoactive materials and electrodes on a conductive fiber and showed a multilayered core-sheath structure. In other words, if such wire cells are unzipped along the axial direction, they produce planar devices. Therefore, similar to planar devices, the photoactive materials can be closely contacted with two electrodes, and high energy conversion efficiencies are expected from the core-sheath design in an ideal model. Cao and co-workers had made an important advancement in the wire cell.¹⁴ They fabricated a DSC wire by wrapping a layer of carbon nanotube (CNT) film on a modified titanium wire grown with titania nanotubes and coated with photoactive materials. CNT has been widely explored as a promising material for various electrodes due to the remarkable electrocatalytic activity, high electrical conductivity, low-cost and easy fabrication.^{15,16} Here the CNT layer was used as a counter electrode while the modified titanium wire served as the working electrode. The resulting DSC showed an efficiency of 1.6%, which were further improved to 2.6% with the assistance of a second conventional metal wire (silver or copper). Currently, it is rare for the DSC wire with core-sheath architecture possibly due to the fact that liquid electrolytes are mainly used. It is not easy to make an effective and stable outer electrode on a liquid electrolyte during the fabrication.

2.2. Twisting architecture from two fibers

The wire-shaped DSCs have been mostly fabricated by twisting two conductive fibers as electrodes, and the one as a working electrode is coated with photoactive materials such as dye and semiconducting metal oxide. In this case, the two electrodes can be easily connected to an external circuit. Here at least one fiber electrode is required to be flexible. Otherwise, the two fibers cannot be effectively twisted to guarantee stable performances. Therefore, the main efforts have been paid to studying different types of fibers for both working and counter electrodes. Currently, metal wires, optical fibers, carbon fibers and carbon nanotube fibers represent the most studied materials.

2.2.1. Metal wires as both working and counter electrodes. A platinum wire is generally used as a counter electrode due to the high electrocatalytic activity for the electrolyte in DSCs, while the working electrode may be made of various metals such as titanium and steel coated with a layer of semiconductive metal oxide.^{10,17-24} Zou and co-workers had pioneered this direction previously by twisting a steel wire coated with porous titania and a platinum wire coated with protective polymer layer (Fig. 5).¹⁰ The open voltage (V_{oc}) , current density (I_{sc}) and fill factor (FF) were 0.61 V, 1.2 mA cm⁻² and 0.38, respectively, and the energy conversion efficiency (η) was calculated as 0.27%. In order to improve the photovoltaic performance, they further used a titanium wire coated with a layer of titania nanoparticles to replace the porous titania-modified steel wire. A much higher efficiency of 5.41% had been achieved.¹⁷ With the assistance of a parabolic-shape reflector to effectively harvest the diffusive



Fig. 5 A typical wire-shaped DSC by twisting two steel wires. (a) Photograph. (b–d) SEM images. Reprinted with permission from ref. 10. Copyright 2008, John Wiley and Sons.

light in all directions, the efficiency had been further increased to 7.02%.¹⁸

Titania nanoparticles show a high interface area which will decrease the charge transport efficiency. Therefore, aligned titania nanotubes were recently perpendicularly grown on the fiber electrode to replace their nanoparticles, and the produced charges could more rapidly transport along the nanotube length with much shorter pathways.^{19–21} To this end, the shorter are the titania nanotubes, the higher efficiency the wire cell can achieve. However, a certain length is required for the effective infiltration of dye molecules and electrolytes. There exists an optimal length for the titania nanotube. Liu and Misra had compared the wire cells with different lengths of titania nanotubes, and the maximum efficiency occurred at a length of 55 µm.²² This value may vary, depending on the used photoactive material and electrode. The thread pitch also plays a critical role on the efficiency of the wire cell. Meng and co-workers had prepared a reel equipment to fabricate wire cells with controlled thread pitches, and the optimal thread pitch was found to be 1 mm.²³ Currently, the maximum efficiency based on titania nanotubes exceeds 7%. More efforts are still required to improve the quality of titania nanotubes as there exist a lot of defects which largely decrease the charge transport.

Besides the direct twist of two fiber electrodes, the other modified structure had also been explored. For instance, Liu and co-workers had successfully developed a wire cell with threedimensional architecture by using a spiral-shaped titanium wire as a working electrode (Fig. 6).¹⁹ It was shown that liquid electrolytes could be more incorporated into the device due to a capillary force, and an efficiency of 4.1% was obtained. Although this structure design is attractive, the resulting device showed limited flexibility based on the used electrode, which may limit the use in many flexible structures.

2.2.2. Metal-free fiber as working electrode with platinum wire as counter electrode. Besides metal wires, the other fiber materials had been also widely explored for working electrodes, *e.g.*, carbon fibers are proposed as a promising candidate due to the combined high thermal stability, mechanical strength and electrical conductivity (Fig. 7a).²⁴ However, the resulting device exhibited an efficiency of 1.28%, which was currently much lower than the conventional titanium wire (Fig. 7b). In addition, here the counter electrode was composed of a glass substrate coated with Pt or a Pt-coated tube, so these wire cells were not flexible and weaveable.



Fig. 6 A wire-shaped DSC based on a three-dimensional architecture. Reprinted with permission from ref. 19. Copyright 2010, IOP Publishing.



Fig. 7 A wire-shaped DSC based on carbon fiber and titania nanorods. (a) Schematic illustration. (b) Current density–voltage curves. Reprinted with permission from ref. 24. Copyright 2012, American Chemical Society.

Engineering fibers and many other commercial fibers are not electrically conductive and cannot be directly used as electrode materials. However, after modifications with conductive materials, they may represent another promising candidate for the working electrode due to the unique advantage, e.g., the sunlight can effectively transport inside. Wang and co-workers had designed and prepared zinc oxide nanowire arrays on the optical fiber with a three-dimensional structure, which not only reduced the shadow effect produced in the twisted fiber electrode but increased the interaction area between light and dye molecules (Fig. 8a).¹¹ In other words, the incident sunlight along the axial direction of optical fiber could be reflected to create multiple opportunities for energy harvest and conversion at the interface. The efficiency had achieved 3.3% when the light was illuminated along the axial direction in the optical fiber (Fig. 8b), about six times of the same device if the light was illuminated outside as generally used. The efficiency had been further increased to 5.64% when a platinum-coated stainless steel was used as the counter electrode.²⁵

2.2.3. Metal wire as a working electrode with metal-free fiber as a counter electrode. Platinum wire is generally used as a counter electrode due to a high electrocatalytic activity towards the redox reaction of I^-/I_3^- electrolyte. However, the high cost and low flexibility has largely limited the practical application and performance improvement of wire cells.^{14–16,26} To this end, carbon-based fibers such as carbon fiber and carbon nanotube fiber which exhibit high flexibility, high conductivity and low cost have been widely investigated as new and promising candidates in the replacement of platinum wire. A carbon fiber as a counter electrode was twisted with a Ti wire which had been coated with a layer of porous titania on the surface (Fig. 9), and an efficiency

of 2.7% was achieved.²⁶ After the carbon fiber was platinized and combined with a stainless steel wire, the efficiency can be further increased to 5.8%.

To improve the practical application, CNTs have been widely spun into fibers in which the CNTs are highly aligned to extend their excellent properties from nanoscale to macroscopic scale.15 For instance, these CNT fibers show electrical conductivities of $10^2 - 10^3$ S cm⁻¹ and tensile strengths of $10^2 - 10^3$ MPa. They are more flexible than carbon fibers and various other available fiber materials such as metal wires and modified engineering fibers. In addition, the designed nanostructure provides a higher interface area which favors the charge separation and transport. The CNT fibers can be continuously made at a large scale with tunable diameters from several to tens of micrometers. The above combined unique advantages enable an ideal candidate for the wire-shaped solar cell. For instance, a CNT fiber was used as the counter electrode and twisted with a titanium wire modified with titania nanotubes (Fig. 10).¹⁵ The wire efficiency achieved 4% without assistance of any metal wire. In addition, the aligned CNT fiber was found to show higher electrocatalytic activity than the conventional platinum wire mainly due to a much higher surface area.¹⁵ If platinum was also made at a nanoscale such as nanoparticles, they showed higher electrocatalytic activity than the other candidates including CNTs. For instance, when a CNT fiber modified with platinum nanoparticles was used as the counter electrolyte, a higher efficiency of 4.85% was obtained even CNTs were not highly aligned in the composite fiber.16 Note that the alignment of CNTs is important for their optoelectronic applications as charges have to cross many more boundaries if they are randomly dispersed.^{27,28}

Chemical fibers can be also used for counter electrodes after modification with a conductive layer on the surface. For instance, conventional threads had been coated with a conductive poly-(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) layer and then used to fabricate wire-shaped DSCs.²⁹ Due to the high electrical conductivity and electrocatalytic activity, the resulting wire cell showed a high efficiency up to 4.8%.

2.2.4. Metal-free fibers as both working and counter electrodes. Compared with metal wire substrates, metal-free fibers such as the mentioned carbon fiber and CNT fiber are light-weight, flexible and stable. Therefore, if both working and counter electrodes are made of metal-free fibers, they may better meet the



Fig. 8 A wire-shaped DSC based on optical fiber and zinc oxide nanowires. (a) Schematic illustration. (b) Current density–voltage curves. Reprinted with permission from ref. 11. Copyright 2009, John Wiley and Sons.



Fig. 9 A wire-shaped DSC by twisting carbon fiber as a counter electrode on Ti wire as working electrode (a) Schematic illustration. (b) Photograph. (c) SEM image of carbon fibers. Reprinted with permission from ref. 26. Copyright 2011, The Royal Society of Chemistry.



Fig. 10 A wire-shaped DSC by twisting two carbon nanotube fibers. (a) Schematic illustration. (b) SEM image of the flexible carbon nanotube fiber. (c–e) SEM images. Reprinted with permission from ref. 15. Copyright 2012, John Wiley and Sons.

requirements of practical applications in the future. Zou and co-workers developed an all carbon fiber-based DSC in which a commercialized carbon fiber coated with a sensitized nanocrystalline titania layer functioned as the working electrode while another carbon fiber coated with ink carbon served as the counter electrode.³⁰ This wire-shaped DSC exhibited an efficiency of 1.9%.

Similarly, aligned CNT fibers had been also used to fabricate the metal-free DSC.^{13,31} As shown in Fig. 11a and b, one CNT fiber coated with a titania layer was used as the working electrode with another bare CNT fiber as the counter electrode. The two CNT fiber electrodes could be tightly twisted with a close contact between them, which proved critically important for the high performance (Fig. 11c–e). Three photovoltaic parameters of V_{oc} , J_{sc} and FF were obtained as 0.64 V, 9.03 mA cm⁻² and 0.45, respectively, which produced an efficiency of 2.60%. In addition, the main photovoltaic parameters remained almost uncharged with the increase of cell length from 0.4 to 1.2 cm (Fig. 11f). In other words, these wire cells show the potential to be scaled up. As expected, the wire structure provides the cell with another unique advantage, *i.e.*, the cell efficiency is independent on the incident light angle (Fig. 11g).

2.3. Solid-state DSC wires

The discussed wire-shaped DSCs were mainly fabricated on the basis of liquid electrolytes. This may bring some problems on the stability and safety during the practical application. It remains challenging to seal the wire cell, and it is also easy for the electrolyte to leak and volatilize in the use, particularly, under bending after the photovoltaic wire is woven or integrated into other structures. Therefore, it is necessary to develop wire-shaped DSCs without using liquid electrolytes though only a few of reports are available.^{32,33} Mainly, cupric iodide was used as the solid-state electrolyte to fabricate the desired DSC wire (Fig. 12a and b), and the efficiency was relatively low at 1.38% (Fig. 12c).³³



Fig. 11 A wire-shaped DSC by using carbon nanotube fiber and modified titanium wire as counter and working electrodes. (a and b) Schematic illustrations from side and top views, respectively. (c–e) SEM images. (f and g) Dependence of V_{ocr} , J_{scr} FF and η on the cell length and incident light angle, respectively. Reprinted with permission from ref. 13. Copyright 2012, American Chemical Society.



Fig. 12 A wire-shaped DSC with a solid-state photoanode. (a) SEM image without (left) and with (right) counter electrode. (b) Photograph with a length of 30 cm. (c) *J–V* curves of Ti wire-based and steel wire-based DSCs. Reprinted with permission from ref. 33. Copyright 2011, The Royal Society of Chemistry.

3. PSCs in a wire format

Compared with wire-shaped DSCs, wire-shaped PSCs do not require electrolytes and could be more easily sealed with higher safety and scaled up with low cost. Similar to DSCs, PSCs could also be fabricated with both core-sheath and twisting architectures according to the application requirement.

3.1. Core-sheath architecture based on a single fiber

Optical fibers have often been studied as substrates in the coresheath architecture as the incident light could be "waveguided" into the photoactive layer along the axial direction.^{34–38} A typical structure of such a PSC wire is schematically shown in Fig. 13a.³⁵ The conductive indium tin oxide layer and photoactive layer of poly(3-hexylthiophene) (P3HT) or poly(3-hexylthiophene):[6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) were sequentially coated on the optical fiber by a dip-coating process, and the aluminum layer was then deposited on the outer surface by thermal evaporation method. Compared with the planar counterpart, the reflective and transmissive losses can be minimized (Fig. 13b), and an efficiency of 1.1% was obtained (Fig. 13c). Besides the optical fiber, modified plastic fibers such as polyimide-coated silica fiber and polypropylene fiber had been also used as the fiber substrate in PSCs, but the coated conductive metal layers are required to be less than 20 nm in thickness for the transmission of the incident light.³⁹

Recently, single-walled CNT films were shown as counter electrodes to produce wire cells with higher efficiencies (Fig. 14).⁴⁰ The wire cells were fabricated by the use of functional multi-layers on the surface of steel wires. A zinc oxide nanocrystal layer with thicknesses of about 40 nm were first deposited as a holeblocking layer. It also helped to stabilize the following casting of the photoactive P3HT and PCBM layer. A poly (3,4-ethylenedioxythiphene):poly (styrenesulfonate) layer with thicknesses of 40–60 nm were then coated to improve the hole transport and electrical contact to the transparent counter electrode, a thin layer of single-walled CNTs. Here the thickness of P3HT:PCBM was critical to the cell performance. When it ranged from 150



Fig. 13 A wire-shaped PSC based on an optical fiber. (a) Schematic illustration. (b) Light illumination, propagation and confinement inside the active medium through reflection from AI, and refractive index difference between the layers. (c) Dependence of the current density and efficiency on incident angles with respect to the axis of the optical fiber with diameter of 1.5 mm. Reprinted with permission from ref. 34. Copyright 2007, American Institute of Physics.

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Fig. 14 Fabrication of wire-shaped polymer solar cells with two architectures. Reprinted with permission from ref. 40. Copyright 2012, American Chemical Society.

to 180 nm, the photovoltaic wire showed high efficiencies of 2.26–2.31%, which was close to 2.48% for their planar counterparts under the same conditions. The cell efficiency showed a drop decrease to about 1% when the layer was thinner than 100 nm or thicker than 200 nm.

3.2. Twisting architecture from two fibers

Wire-shaped PSCs had also been widely explored by twisting two fiber electrodes. For instance, Gaudiana and co-workers demonstrated that two metal wires were twisted to form wire cells.¹² However, it is generally difficult for two metal electrodes to be closely twisted. To this end, flexible CNT fibers had been recently developed as one electrode and twisted with a titanium wire which was grown with a layer of titania and coated with photoactive materials (Fig. 15a).⁴¹ The two electrodes could be closely contacted, but the resulting PSC wire showed an efficiency of 0.15% (Fig. 15b). The relatively low efficiency may be ascribed to the fact that the incident light cannot be absorbed by the photoactive layer due to the thick titania nanotube arrays. Another possible reason is derived from a mismatch of the energy level for the used photoactive material. As a modification, when a CNT fiber was twisted with a modified steel where a zinc oxide nanocrystal layer as a hole-blocking layer and poly(3,4-ethylene-dioxythiphene):poly(styrenesulfonate) for the improvement of hole transport, the resulting wire cell showed a much higher efficiency of 2.11%.⁴⁰ In addition, they had further compared the twisted polymer wire cells by using silver wire as the counter electrode under the same condition. A much lower efficiency of 0.8% was obtained. As previously mentioned, fiber substrates were found to play a critical role on the performance of wire cells. If a metal wire such as aluminum wire was used to fabricate twisted polymer



Fig. 15 A CNT fiber-based PSC. (a) Schematic illustration. (b) *J–V* curves, respectively. Reprinted with permission from ref. 41. Copyright 2012, The Royal Society of Chemistry.

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Fig. 16 SEM images of a polymer photovoltaic wire by using aluminum wire in replacement of the CNT fiber. (a) Low magnification (the inserted image showing the surface of an aluminum wire). (b) and (c) Higher magnifications of (a) at different locations. Reprinted with permission from ref. 41. Copyright 2012, The Royal Society of Chemistry.

wire cells in replacement of the CNT fiber, obvious gaps were observed between two electrodes (Fig. 16).⁴¹

In fact, for both PSCs and DSCs, although CNT fibers were shown as promising fiber substrates, the properties of CNT fibers need to be further improved. Recently, the formation of composite fibers had been proved as an effective route.^{42–44} For instance, nitrogen-doped CNTs had been introduced and found to largely enhance the electrocatalytic activity of fibers mainly due to the electron-accepting nature of nitrogen atoms which produced positive charges in neighboring carbon atoms to attract electrons from the anode.⁴² A wide variety of other materials including metal/ metal oxide nanoparticles and conductive polymers had also been electrodeposited onto CNT fibers.⁴⁴ The resulting composite fibers exhibited much improved electrical conductivities, mechanical strength and electrocatalytic activities. More efforts should be paid to developing these composite fibers for wire-shaped solar cells with higher performances.

4. Main challenges and directions of wireshaped solar cells

There remain many challenges in wire-shaped solar cells although great achievements have been obtained in recent years. For both wire-shaped DSCs and PSCs, the efficiencies are still much lower than their counterparts in the conventional planar format. In particular, the lengths of available wire-shaped DSCs and PSCs ranged from several to tens of centimeters. With the further increase of the cell length to an application level, the efficiencies will be largely decreased to very low values as the electrical resistances of fiber electrodes are linearly increased. It currently remains challenging to reach a balance between high efficiencies and acceptable lengths. To this end, the fiber electrodes with high electrical conductivities are critically important to develop usable wire-shaped solar cells.

Some specific problems exist for each type of wire cell. Liquid electrolytes are mainly used for the wire-shaped DSC. For the planar structure, it is unfavorable but not difficult to seal a DSC. However, it is difficult to seal a wire cell at a large scale. Even available in the future, the cost will be much increased, and the safety will also be another big challenge. Therefore, more efforts should be paid to solid-state electrolytes, though no reports are available for wire-shaped DSCs along this direction yet. PSCs are more suitable for a wire structure as solid materials are always used. However, there are only a few reports possibly due to the difficulty in the interface control between two electrodes. For instance, the requirement of a thin photoactive layer often leads to a short circuit in a core-sheath structure, while a low contact area between two fiber electrodes is unfavorable for a rapid charge separation and transport in a twisted structure.

There also remain some technical challenges in the fabrication of wire-shaped solar cells. For a core-sheath structure, it is difficult to coat uniform and thin photoactive and electrode layers on a fiber substrate, particularly, at a large scale based on the current fabrication technology. For a twisting architecture, it is difficult to wind two fiber electrodes in a well tunable and repeatable process. It is also difficult for two fiber electrodes to be closely and stably intertwined during the use. In addition, a promising advantage of wire-shaped solar cells lies in that they can be woven into clothes or other flexible structures. However, it remains unclear how the electrodes are connected to collect the electric power for so many wire devices. To the best of our knowledge, no attempts have been even made to address this concern and develop technologies for such organizations.

Besides the described directions to solve current scientific and technical challenges of wire-shaped solar cells, a new and promising development has been recently attempted for the device integration. Generally, the solar energy is converted to



Fig. 17 (a and b) Schematic illustration of the circuit connection during charging and discharging processes, respectively. (c) Charging-discharging curve of a typical wire with the current of 0.1 μ A during the discharging process. Reprinted with permission from ref. 47. Copyright 2012, John Wiley and Sons.

electric energy and then stored by electrochemical devices such as lithium ion batteries and supercapacitors through external electric wires. To further improve the energy conversion and storage efficiency, it is critically important to simultaneously realize the two functions, *i.e.*, photoelectric conversion (PC) and energy storage (ES), in one device. Recently, attempts are made to directly stack a photovoltaic cell and a supercapacitor or integrated them into one which can absorb and store solar energy.^{45,46} Integrated energy wires are made to simultaneously achieve PC and ES.

As a demonstration, CNT fibers are shown here to produce integrated energy wires.47 For the titania nanotube-modified parts on a titanium wire, photoactive materials are dropped onto some for PC, while a gel electrolyte was coated onto the others for ES. CNT fibers were then twisted with both PC and ES parts to produce an integrated wire-shaped device. Here titanium wire and CNT fibers have been used as electrodes. The energy wire would be charged upon exposure to the light when the PC and ES parts were connected (Fig. 17a). The voltagedischarge was conducted when the PC and ES parts were disconnected (Fig. 17b). The voltage change during the charging and discharging was carried out by connecting the ES part with a potentiostat. Fig. 17c shows the charge and discharge curves when the energy wire had been exposed to the light irradiation. The energy conversion efficiency was calculated to be 2.2% similar to the wire-shaped DSC, and the storage efficiency was found to be 68.4%. As a result, this novel wire device exhibits an entire photoelectric conversion and storage efficiency of 1.5%.

Conjunctional harvesting of energy from multiple sources in a single device represents another new trend in energy technologies, and the integrated device for harvesting solar and mechanical energy has been explored typically in a planar format. Wang and co-workers had pioneered this design conception to wire-shaped devices (Fig. 18a).⁴⁸ They showed that an optical fiber-based integrated device was composed of a DSC for harvesting solar energy and a nanogenerator for harvesting mechanical energy. These active materials were fabricated coaxially around a single optical fiber as a coresheath structure. For a series connection (Fig. 18b), the $V_{\rm OC}$ values of DSC and nanogenerator were ~ 0.4 and 2.9 V, respectively, so the integrated wire showed an entire $V_{\rm OC}$ of 3.3 V, the sum of two individual cells. For a parallel connection, the $I_{\rm SC}$ values of DSC and the nanogenerator were 7.52 and 0.13 μ A,



Fig. 18 An optical fiber-based integrated cell consisting of a DSC and a nanogenerator. (a) Schematic illustration. (b) Open-circuit voltage of the integrated wire when the nanogenerator and the DSC were connected in series. Reprinted with permission from ref. 48. Copyright 2012, John Wiley and Sons.

respectively, and an entire $I_{\rm SC}$ of 7.65 µA, also the sum of two individual cells, was produced. Therefore, a series of DSCs and nanogenerators may be easily assembled into highly integrated wire devices depending on the application.

5. Conclusions and outlook

Due to the unique advantages (*e.g.*, light weight, weavability and ease to be integrated) *versus* planar solar cells, wire-shaped organic solar cells have attracted extensive attention after they were firstly fabricated a few years ago. Great advancements have also been made despite of the relative short history. To summarize, two main architectures have been widely investigated, and various fiber substrates which are critically important to the wire-shaped device have been extensively explored. The maximum energy conversion efficiencies have currently exceeded 7%.

In the case of different solar cells, a few critical scientific issues still need to be addressed. For the DSCs, more efforts are required to develop solid-state electrolytes which are particularly important for a wire cell to improve the stability. For the PSCs, it is urgent to understand the impact of the electrode interface on the performance of wire cells aimed at increasing the efficiencies which are currently much lower than their planar counterparts. For both DSCs and PSCs, it is necessary to further explore new electrode and photoactive materials and optimize the cell structure (*e.g.*, preparation of active layers and assembly of electrodes need to be improved), and develop technologies to scale up the fabrication process as the reported devices were still limited to centimeters.

Wire-shaped solar cells can be easily integrated into multifunctional devices, *e.g.*, the simultaneous realization of photoelectric conversion and energy storage and simultaneous conversion of solar and mechanical energy.^{47,48} They may be also integrated with other energy conversion and storage parts to produce new and efficient devices. To this aim, more efforts should be paid to optimize the structure and enhance the performance of integrated wires.

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