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Review

Fiber-shaped flexible solar cells

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ABSTRACT

Flexible solar cells with the advantages of lightweight, foldability, and low cost, and extensive applications have attracted much academic interest and industrial attention during the last decades. The principles, development, and characteristics of various silicon based, CuInGaSe, dye-sensitized, and organic photovoltaic flexible solar cells are introduced and reviewed. Special emphasis gives different types of the newly and rapidly developed fiber-shaped solar cells and their characteristics. Compared with traditional ones, the fiber-shaped solar cells use flexible photoelectrodes prepared with low-cost metal wire, optical fibers, and carbon etc., not only greatly expanding their flexibility and decreasing cost, but evidently improving their various properties. At last as their further development, some prospective researches on mesh-like solar cells are introduced.

1. Introduction

1.1. Background

With continuous reduction of fossil fuel resources and more and more stringent restrictions for greenhouse gas emissions, human ever-increasing demand for energy forces people to seek highly effective inexhaustible energy sources. Solar energy, with many advantages such as large reserve, sustainable utilization, environment-friendly nature, is no doubt the preferred and optimal. Converting sunlight into electricity is one way to effectively use solar energy, because electricity is the basic input form of energy for most energy-consuming equipments and has superior advantages for the long-range transmission, easy storage etc. Solar cells, as the devices to convert solar energy to electrical one, have been developing very rapidly.

1.2. Principles and structures of various solar cells

A solar cell is the device that can directly convert solar energy into electrical energy. There are many kinds of photovoltaic mate-

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rials: silicon based materials including crystalline, polycrystalline, and amorphous silicons, compound semiconductor materials including GaAs and $CuInSe_2$ (CIS), and so on. The working principle of silicon solar cells is based on the p–n junction of the photovoltaic effect: n-type and p-type semiconductors with certain structures form a p–n junction at their interface, where forming a space charge area due to diffusion of majority carriers and an ever-growing built-in electric field directing from the n-type region to the p-type region, leading to reverse drifting of the majority carriers and finally reaching equilibrium. The current produced by diffusion equals to that produced by drifting after equilibrium. When light falls at the p–n junction and the energy of incident photon is higher than the band gap energy of the material, electron–hole pairs form in the vicinity of the p–n junction. Driven by the built-in electric field, non-equilibrium electron-carriers will diffuse toward both ends of space-charge region to create light-induced electric potential, resulting in destruction of the original balance. When electric circuit is formed by connecting electrodes on both sides of the cells with a load, an available power can be obtained.

In 1976, Carlson and Wronski of RCA Laboratory in the United States jointly developed the first silicon thin-film solar cell [1], which declared a new era of thin-film photovoltaic technology. However, the development of monocrystalline silicon solar cells was greatly hindered due to the high expense and the difficulty in producing them on large area non-silicon substrate. Thin-film polycrystalline silicon solar cells (PSSCs), though having stable performance and high conversion efficiency, usually need a long heat treatment and borosilicate glass or ceramic substrates with high-temperature-resistance, therefore face great technical challenges to improve the material performance.

Developed in the 70s of the 20th century, the $CuIn_xGa_{(1-x)}Se_2$ (CIGS) thin-film solar cell is the polycrystal compound semiconductor heterojunction one. Its principle is similar to the Si-based one, works based on the p–n junction photovoltaic effect. Unlike the silicon cells based on a homojunction, the structure of CIGS cells is a more complex heterojunction system. As early as in 1974, Wagner and others studied the n-type cadmium sulfide (GeS) and p-type copper indium selenide (CIS) solar cell, its power conversion efficiency was as high as about 12% [2]. A team at the U.S. National Renewable Energy Laboratory (NREL) achieved 19.9% new world record efficiency by modifying the CIGS surface and making it look like CIS [3]. At present, CIGS thin-film photovoltaic cells have been more maturely developed, but are limited by such problems as the limited reserves of indium, gallium, and selenium, the difficulty preparing high-purity semiconductor materials, and so on. Therefore, there are certain concerns for raw material supply in their large-scale applications. In the development of a new generation photovoltaic cell, dye-sensitized solar cells (DSSCs) and polymer organic photovoltaic cells become two hot spots of concern. M. Grätzel, Prof. of Federal Institute of Technology, Lausanne, Swiss, has made pioneering researches in the DSSC field since the 80s of last century [4–7]. By utilizing a new type of porous nanocrystal titanium dioxide (TiO_2) thin-film electrode sensitized with ruthenium dye that has strong light absorption on TiO_2, and a suitable redox electrolyte, He developed a highly efficient DSSC, greatly increasing its efficiency from less than 2% to more than 7%. It has been increased to more than 11% in recent years after optimization [8]. DSSC mechanism mimics that of the process of photosynthesis, as shown in Fig. 1. The dye molecules are transited from the ground state to the excited state after absorbing light, and then an electron is rapidly injected into the conduction band of semiconductor film (typically TiO_2 thin film). In the side of the counter electrode, the I^{3-} is reduced by an electron to I^-, which in the end transfers the electron to the dye molecule that has lost one electron to complete the regeneration of dye.

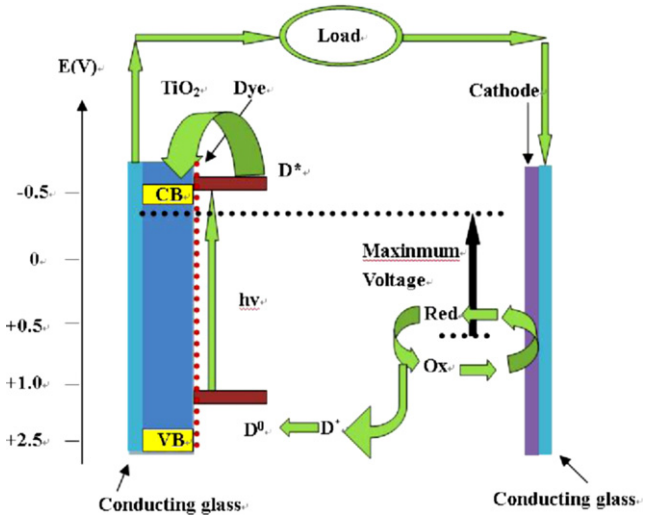

Fig. 1. Schematic of DSSC.

The advantages of DSSCs lie in its simple production method, varieties of material sources, low cost, non-toxicity, and most importantly, extensive applications. Compared with other solar cells, DSSCs have higher efficiency even under weak light condition, so they can be used to provide electricity to indoor equipments such as laptops, mobile phones, etc. They can also be fabricated on flexible substrates such as plastic or metallic thin films to achieve large-area and roll-to-roll production. Similarly, organic photovoltaic (OPV) cells have advantages of rich sources, low cost, and easy control of molecular structures of materials. Moreover, organic materials are flexible; therefore they can be continuously produced through low-cost wet film-forming processes such as spin-coating, ink-jet printing, and roll-to-roll etc., and are expected to develop bendable and foldable new photovoltaic devices to bring great convenience in use. In recent years, OPV cells have attracted great academic interest, and also have drawn enormous investment from the industrial community to achieve real practical application.

Bulk heterojunction structure is the predominant structure of polymer solar cells [9–12], as shown in Fig. 2. In 1994, Yu et al. made the first bulk heterojunction solar cells by mixing MEH-PPV and C_{60} [13,14]. Different from inorganic photovoltaic cells which directly generate free electrons and holes, in OPV cells, after absorbing photons of specific energy, electrons at the level of the highest

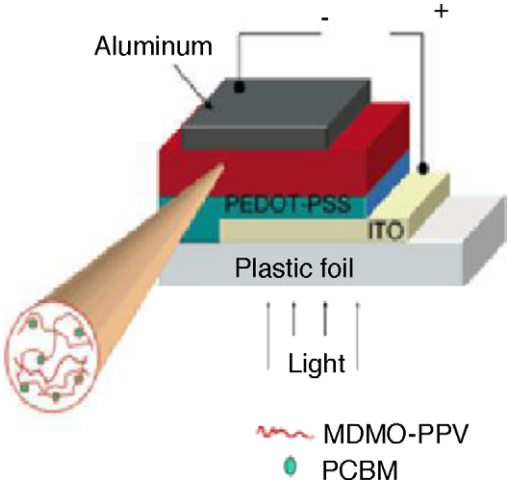

Fig. 2. Bulk heterojunction configuration in the organic solar cell. Reproduced from Ref. [9].

occupied molecular orbital (HOMO) in the conjugated polymers will transit to the level of the lowest unoccupied molecular orbital (LUMO), at the time producing holes at HOMO orbit. Because of their smaller dielectric constant and intermolecular interaction of polymers, electrons and holes generated by light excitation will be present in the form of electron–hole pairs or excitons due to the strong binding energy between them. Excitons diffuse and reach the interface of donors and acceptors, where the separation of photo-induced charges occurs: electrons transfer to the LUMO of the receptor while holes to the HOMO of the donor. Driven by potential barrier, holes and electrons are respectively transmitted to the anode and cathode, completing charge collection and forming electric current. In the polymer heterojunction solar cells, the films are prepared by spin-coating the mixture of donor and acceptor materials. The nano-scale, bicontinuous interpenetrating network bulk heterojunction structure greatly increases the interface area between the donors and acceptors and effectively separates excitons before quenching. Meanwhile, holes and electrons transmit in the continuous phase of donors and acceptors, respectively, by which greatly improves the efficiency of solar cells [15–18].

1.3. Flat flexible solar cells

Restrictions of traditional rigid (silicon, conductive glass, etc.) greatly limit transportation and applications of flat solar cells. Therefore, development of solar cells based on flexible substrates becomes another hot focus following traditional cells. As early as 1967, flexibilization of silicon solar cells was proposed to reduce their thicknesses and at the same time to replace traditional solid substrates with flexible plastic substrate for the purpose of flexible silicon solar arrays [19]. In 1976, the birth of amorphous silicon thin-film solar cells proclaimed the advent of thin-film solar cells and provided the basis for flexibilization of silicon-based solar cells. Silicon-based thin-film solar cells include polycrystalline and amorphous silicon solar cells. In 1990, Kishi and co-workers [20] fabricated the world's first flexible amorphous silicon solar cell on a transparent plastic substrate. Although its thickness is only 0.12 mm and bending radius is only 5 mm, the cell had the world's highest calorific value of 275 mW/g at that time. The amorphous silicon material has very high absorption coefficient. Hence, sunlight can be completely absorbed within less than 1 μm thickness and cost can be reduced. However, the existence of bandtail states in its forbidden bands, together with other factors such as dangling bands and stress bonds will affect transmission of carriers in solar cells, and because of the Staebler–Wronski effect (SWE), amorphous silicon alloys can be degraded under illumination [21]. In order to alleviate these problems, multi-junction structures are used to reduce SWE through thinner cell structure. In addition, materials with different forbidden bandwidths are applied to improve cells' spectral response and to obtain higher conversion efficiency [22,23]. Most of recent studies focused on polycrystalline and amorphous silicon flexible thin-film solar cells [24], and monocrystalline silicon flexible solar cells have not had a breakthrough before 2008. In April, 2008, Rogers and co-workers [25] reported that they successfully made a scalable deformable and foldable integrated circuit by applying transfer printing technology to monocrystalline silicon nanoband array. Later in the same year, Fan and Javey [26] reported their translucent, flexible, and concentrator-module-designed ultra-thin monocrystalline silicon microcell array fabricated by using transfer-printing technology. This was the first reported monocrystalline flexible solar cell fabricated by using traditional technologies of photoetching and dopping on the bulk silicon. The minimum thickness of microcells can be down to 100 nm, the width a few microns. By wet etching process, the microcell can be hung on the silicon wafer, and then transfer-printed with a soft elastic tape onto other substrates such as plastic or glass. If a reflective layer is fabricated on the silicon wafer of appropriate thickness, the conversion efficiency of the single microcell can be 4–13%.

The characteristics of the work are that most of its production processes, including the high-temperature doping, etching, etc. are performed on traditional monocrystalline silicon chip and then transfer-printed onto the final substrate; the only fabrication process on the substrate is to prepare the metal electrode. Therefore, there is no restriction on substrate materials. Moreover, this method uses the least amount of crystal silicon as light absorption and energy conversion materials, and fully adopts the complete silicon preparation process established already. It can be said that it provides a way to produce low-cost, large-scale industrially produced flexible silicon-based devices including flexible solar cells.

Flexible CIGS solar cells [27] mainly use flexible metal sheets (stainless steel and molybdenum, etc.) and polymers (polyimide, etc.) as their substrates. The key to prepare CIGS on a flexible metal sheet is a good insulating layer between them. Although high deposition temperature is beneficial to active layer deposition, it aggravates diffusion of impurities in the substrate towards the active layer. In order to produce single integrated module, it is necessary to require the substrate with its electrical insulation layer and to keep insulation between the substrate and the active layer without cracks in fabrication processes. These requirements are much stricter than the insulation layer on diffusion of impurities. When using such polymer materials of polyimide-like, there is still an issue of heat-resistance, it is necessary to develop a fabrication process of a high-efficiency active layer at a lower temperature.

Another group of flat flexible solar cells are those based on small organic molecular materials, polymers as well as organic/inorganic hybrid materials. Polymer based solar cells are widely studied as the most potential flexible solar cell because polymer materials have the highest flexibility, film forming ability and mechanical toughness compared with those of other material systems [29]. There are two types of polymer solar cells: the standard type and inverted type [28]. The standard polymer solar cells (as shown in Fig. 3A) has typical structure of indium tin oxide (ITO, anode)/PEDOT:PSS/active layer/metal (cathode). The inverted polymer solar cells have two types as shown in Fig. 3B and C. The structure of the device in Fig. 3B is obtained by exchanging ITO and metal electrode from the standard cell configuration. It can be fabricated by screen printing and is suited to roll-to-roll process. The device in Fig. 3C still uses metal as the canode, but its fabricating process is reversed. First, the metal electrode and then the active layer is coated on the flexible substrate. The two devices have high power efficiency and low cost. Krebs and co-workers reported an inverted polymer solar cell with the structure of substrate-ITO-ZnO-(active layer)-PEDOT:PSS-silver (or aluminum) with P3HT-PCBM as the active layer. The devices with silver as electrode can stably work in the presence of humidity, but not in the presence of oxygen. The inverted device can be entirely fabricated by roll-to-roll process, starting from an olyethyleneterephthalate (PET) substrate solution with an ITO layer. The cells have as high as 2.1% power conversion efficiencies for the full module with 120 cm^2 active area (AM1.5G, 393 $W m^{-2}$) and up to 2.3% for modules with 4.8 cm^2 active area (AM1.5G, 1000 $W m^{-2}$) [30], which is prominent performance for roll-to-roll polymer solar cells. The inversion of the layer sequence is also suited to ITO-free roll-to-roll processing, as recently reported by several groups. Replacing the expensive ITO layer with silver nanoparticles [31] or kapton/Cu/Ti/PEDOT:PSS [32] as electrode and using the so-called wrap through concept [33] to ensure hole contact by letting through PEDOT:PSS are efficient methods to develop ITO-free roll-to-roll processing.

Meanwhile, Krebs group fabricated the large-flexible polymer solar cells by screen-printing [34,35], and its structure is shown in

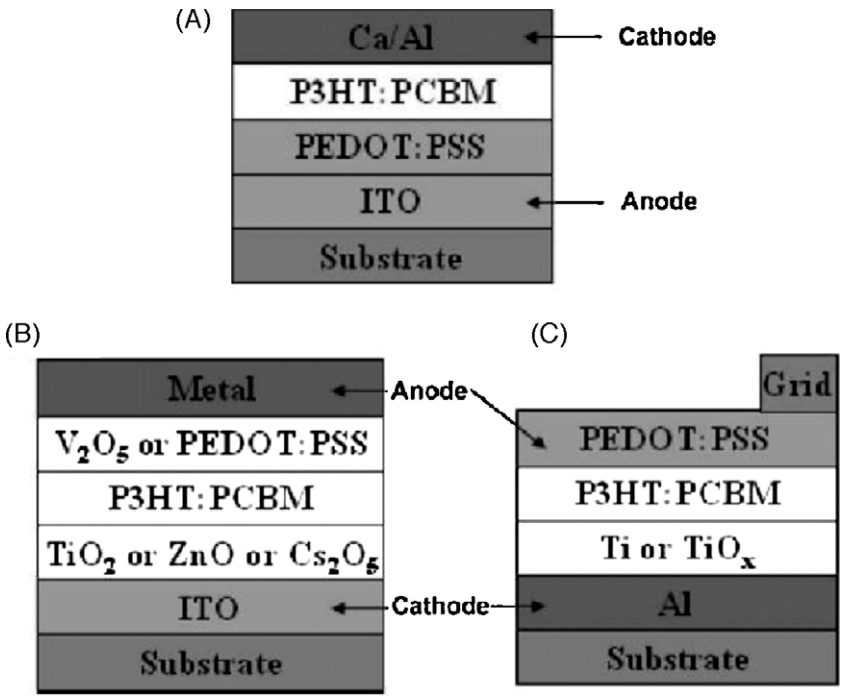

Fig. 3. Architectures of polymer solar cells: (A) standard, (B) inverted (in terms of the roles of the electrodes), and (C) inverted (in terms of the alternative processing structure).
Reproduced from Ref. [28].

Fig. 4. All processings were performed in air without vacuum coating steps, which prominently decrease the cost. The devices gave a power conversion efficiency of 0.2% (1000 W m^{-2}, AM1.5G) and 0.5% (50–100W m^{-2}, AM1.5G). More than four months' study on the devices' stability by eighteen laboratories distributed in Northern America, Europe and the Middle East has demonstrated that it is possible with the current technology to share devices and obtain consistent data even over long periods. The key technology is the barrier material and the encapsulation that gives the devices stability sufficient for studies [36]. Assembling the polymer solar cell modules to the flexible substrates such as textiles provides a potential application of this kind of devices [37].

Because the active layers are flexibile, the study of plate flexible solar cells is focused on how to find suitable flexible materials. In this type of flexible solar cells, polymer substrates are mainly used as flexible substrates to replace glass substrates. These polymers should have good optical, mechanical and chemical properties, such as high optical transparency, large size, mechanical and chemical stabilities, chemical erosion resistance, low thermal expansion coefficient, smooth surface, anti-air and anti-water permeability, and so on. The most widely used flexible substrates are polyester materials covered with ITO or conductive polymers such as poly (3,4-ethylenedioxy-thiophene): poly styrenesulfonate (PEDOT: PSS), polyethylene terephthalate (PET) and polyethylene naphthalate (PEN). In addition, polyester and polycarbonate are also applied [38–47].

The ITO-coated plastic film in DSSC preparation has some problems. Commonly used polyimide-like flexible plastic substrates can withstand high temperature 330 °C, but the poor transparency limits their applications in solar cells. PET substrates has excellent light transmittance, but its highest thermal stability temperature is only 150 °C, which limits TiO_2 thin film heat-sintering during DSSC fabrication because its optimum sintering temperature is 450–500 °C. Researchers have explored a variety of preparation methods of the TiO_2 thin films at low-temperature, such as mechanical suppression [48–51], hydrothermal method [52–54], UV irradiation [55–57], microwave sintering [58], etc. However, the devices developed through these methods not only have lower efficiencies than those through the traditional high-sintering one, but also have higher costs. Researches on solar cells using flexible metal sheets, with their high temperature sintering and high mechanical strength, as the substrates also have been very extensive [59–67,48]. The highest efficiency of DSSC using the titanium plate as its substrate is 7.2% [59]. However, there are many disadvantages which hinder applications of the flexible solar cells, such as the weak cohesional strength of the metal substrates with TiO_2, the big loss caused by light absorption of electrolyte or hole transport layer, etc.

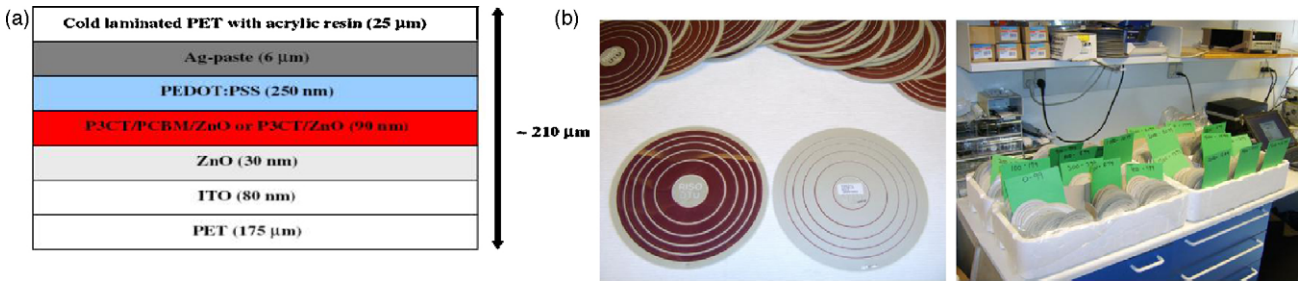

Fig. 4. (a) The structure of the devices. (b) The final modules comprising screen printed layers, back lamination and crimped contacts (left) and all the 2124 modules (right).
Reproduced from Ref. [34].

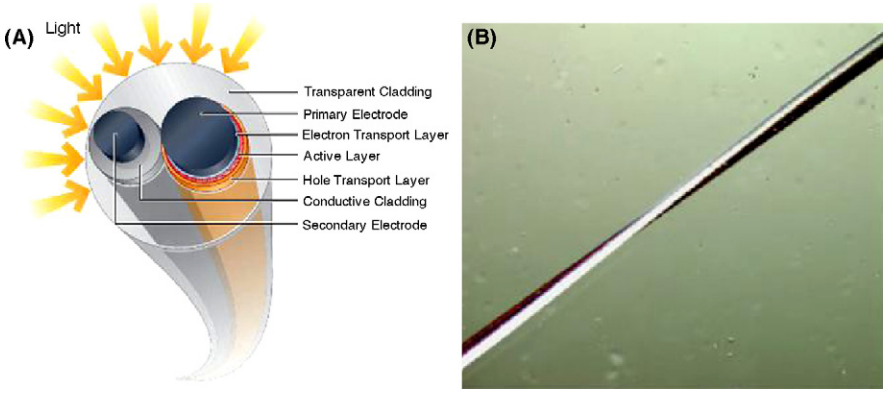

Fig. 5. (A) Schematic of a complete fiber showing the potential for shadowing by the secondary electrode. (B) Optical microscope picture of the silver-coated, secondary electrode wire (white) wrapped around the coated, primary electrode wire before cladding.
Reproduced from Ref. [68].

2. Flexible fiber-shaped solar cells (FFSCs)

The newly developed FFSCs have the active layers fabricated onto their cylindrical substrates. In order to advance the solar cells toward flexible and fibrous, the following methods have been applied: (1) making external light directly radiate on the active layer, (2) injecting light from the optical fiber end into the internal of the solar cells. Applications of these methods have greatly advanced the cell form towards flexibility and fibrousness, and significantly expanded substrate sources. In addition, low-cost and good-conductive metal wire, optical fiber, carbon and other materials have been widely applied to electrode preparation. At the same time, such a structure has the benefits of lightweight and flexibility. Because the fiber length could stretch greatly, which provides more space for large-area devices and makes the stereoscopic cell modules be possible. Most importantly, if the photovoltaic device is built by weaving, then the appearances of photovoltaic cells will be greatly enriched, such weave-like solar cells can be fabricated into clothing, tents, external bond layer of buildings. As the special nature of the fiber cell structures and preparation processes, current studies on fiber cells are primarily focused on organic thin-film solar cells and DSSCs.

2.1. Organic photovoltaic fiber-shaped cells

2.1.1. Optical fiber coated with conductive oxide as anode

During preparation of flexible organic photovoltaic cells, Shtein and co-workers [67] used the semitransparent metal layer as the cell's cathode. Light penetrates from the metal layer into the active layer, thereby reducing the dependency of light on the incident angle. They fabricated the fiber cell with its coatings Mg/Mg: Au/Au/CuPc/C_{60}/Alq_3/Mg: Ag/Ag by high-vacuum depositing on the polyimide silicon wire of 0.48 mm diameter. Under the AM 1.5 standard sunlight, its maximum power conversion efficiency reached 0.50%. Although this device allows light to radiate from the active layer side, its photoelectrode still uses the fiber substrate coated with metal, the manufacturing process is relatively complicated, especially for a longer device. In addition, it is difficult to control the balance between the transmittance and conductivity of its outer layer metal electrode.

2.1.2. Metal wire as anode

Nowadays, there are two main issues in fabricating fiber organic photovoltaic cells. First, as the organic coating layer is very thin, if the electrode surface evenness is not high, it easily leads to short-circuit between two electrodes. In addition, the n-type counter electrode with high conductivity and transparency has not yet been developed, which greatly restricts the performance of a flexible linear photovoltaic device. Gaudiana and co-workers [68] applied the twisting structure to the cells, which greatly improved the device performance. As shown in Fig. 5, they used the stainless wire coated with P3HT/PCBM as the main electrode, and then wrapped another wire as the counter electrode. Using the curved characteristic of the twisting structure, they introduced optical medium layer to change the incident light path and improved the efficiency of light capture. The open voltage of the prepared fiber photovoltaic device was bigger than 0.6 V, the short current was 11.9 mA/cm^2, and the power efficiency was up to 3.27%.

2.2. Fiber-shaped dye sensitized solar cells

2.2.1. Metals as photoanode substrates

Before the work of Zou and co-workers, there were few reports on flexible fiber-shaped organic solar cells and only a few patents on dye sensitized solar cells. For example, one patent pointed out that packaging more than one sensitized TiO_2 electrodes into a transparent tube forms a tubular cell component with a cylinder-working surface. Although this patent referred to the concept of fiber structural TiO_2 electrode, the final diameter and flexibility of the cell were far away from those of the real woven fiber. The structure, shown in Fig. 6, proposed by the patent of U. S. Konarka Inc. is: packaging the fiber working electrodes, and the mixture of filling and electrolyte into the plastic casing whose internal surface coated with transparent conductive oxide operates as its counter electrode, and through the well conductive fiber buried in the transparent conductive oxide wires out the electrodes. Because the special form of its substrate, the processing complexity and cost is higher, and especially, it is a great challenge to form the conductive oxide layer with both good conductivity and transparence in the internal wall of the slender plastic tube. From the structure of the fiber-shaped solar cell mentioned above, it follows that the key to make truly flexible fiber solar

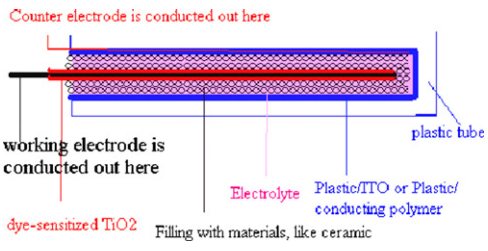

Fig. 6. The structural schematic of patented cells by Konarka.

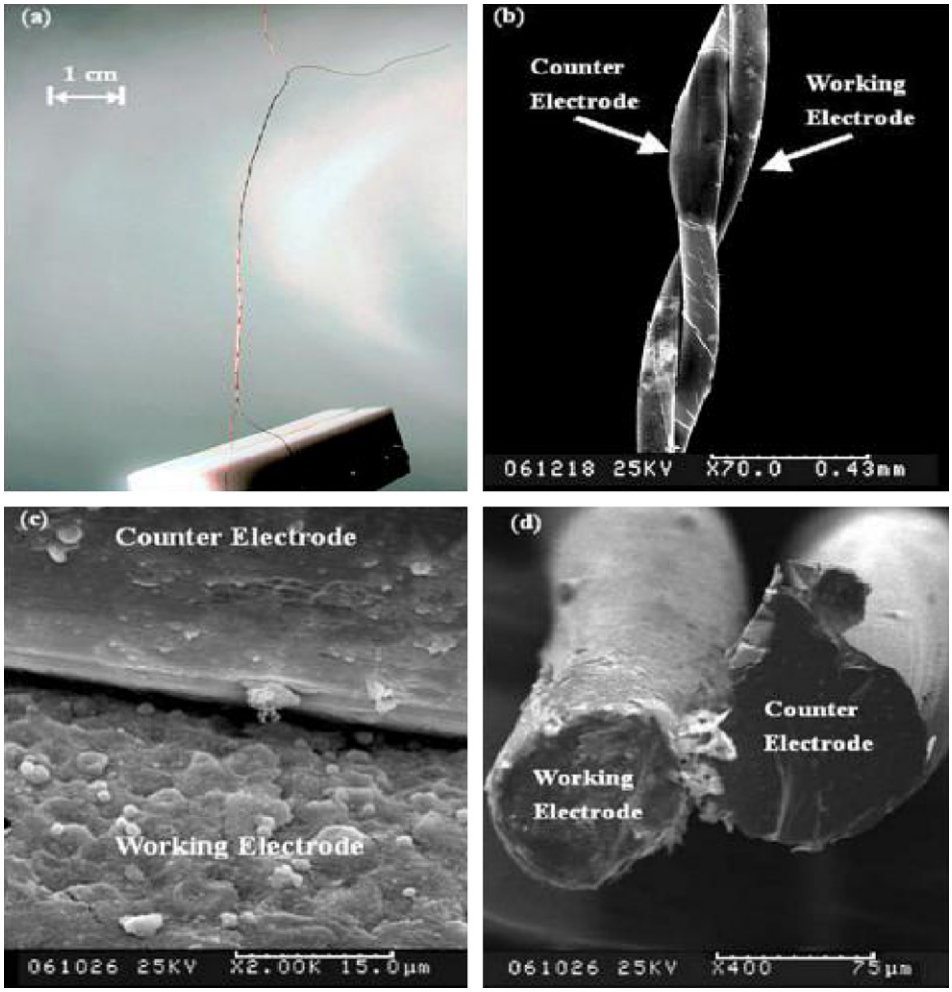

Fig. 7. (a) Optical photo of a twisted Wire-Style-Fiber-DSSC (WSF-DSSC); (b) and (c) SEM photos of a WSF-DSSC (top view); (d) SEM photo of a WSF-DSSC (sectional view). Reproduced from Ref. [69].

cells is how to prepare, on the delicate substrate, the transparent electrode layer to meet the requirement for the cell to harvest light.

Zou and co-workers [69,70] fabricated the TiO_2 thin film by coating method using stainless wire as the substrate. Because of the excellent temperature-resistance of the metal substrate, the TiO_2 thin film can be further sintered at high temperature. Moreover, stainless wire is an inexpensive, lightweight metal with good electrical conductivity. Zou and co-workers obtained the working electrode of diameter less than 100 μm, and further using the gold wire of diameters ranging from ten to several tens micrometers as the counter electrode, assembled their photovoltaic device by directly twisting the working and counter electrodes, the optical photos and SEM photos are shown in Fig. 7. Selection of both the materials and the structure made the fabrication process simple. Since the length can be controlled at will, the device is truly flexible, fibrous, and low cost. The fundamental differences between this device and others are that the nanoparticle light-scattering was used to trap light instead of transparent conductive layer-based light-harvesting approach and no need to consider the transparency of the electrode itself, so the electrode substrate can be very thin. The typical parameters of open circuit voltage (V_{oc}), short circuit current (I_{sc}) and fill factor of the currently reported liquid DSSCs are 610 mV, 1.2 mA/cm^2 and 0.38, respectively. Further improvement for the device's performance is still in progress. It is optimistic to fabricate this solid-state fiber DSSC whose power conversion efficiency is up to 2%.

Titanium is another substrate metal used widely. Huang and coworkers [71] prepared the mesoporous TiO_2 nanowire on the spiral titanium wire and used it as the photoelectrode (shown in Fig. 8) to develop the DSSCs. This type of 3D structure provides an effective transmission path for liquid electrolyte and further increases short-circuit current to 2.3 mA/cm^2, open circuit voltage to 616 mV, and efficiency to 0.86%. However, this helical structure limits the preparation of large area and long devices. In addition, a large volume of electrolyte will cause light loss because of the strong light absorption.

Liu and co-workers [72] used a fibrous titanium wire as the photoanode substrate and a titanium plate as the counter electrode, as shown in Fig. 9. The device's efficiency can reach 5.6%. Although it is not a real fiber cell, using the same titanium as the working electrode and the counter electrode reduces the built-in electric potential strength. Meanwhile, compared with the electrode using FTO as substrate, the high reflectivity of titanium plate increases the scattering-light absorption efficiency up to 53.12%. The study shows that compared with traditional transparent metal oxide electrodes, the metal electrode-based solar cells, which integrate metal wire's high reflectance, high conductivity, high temperature-resistance, and good flexibility, have great advantage.

2.2.2. Fibers coated with conductive oxides as photoanode substrates

Harlin and co-workers [73] made their liquid dye-sensitized solar cell using an optical fiber coated with ZnO: Al as anode and

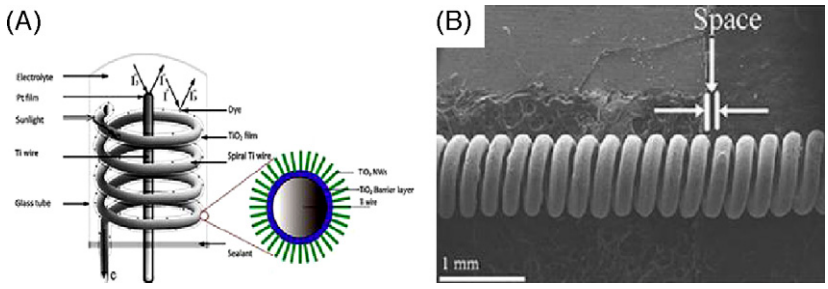

Fig. 8. (A) Design scheme for a 3D photoanode consisting of oriented MTN (macroporous TiO_2 nanowires) grown on a spiral-like titanium substrate (B) Side view SEM image of MTN-substrated photoanode.
Reproduced from Ref. [71].

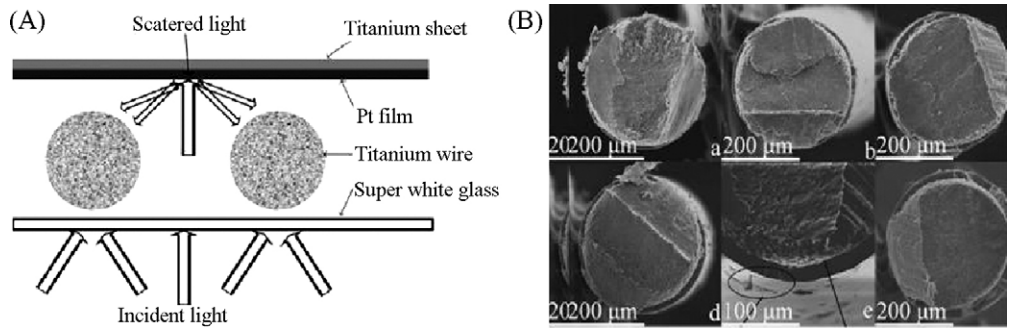

Fig. 9. (A) Schematic of the light path, showing the utilization of incident light in the titanium-based DSSC. (B) SEM images showing cross-sections and the surface morphology of wire-like photoanodes.
Reproduced from Ref. [72].

carbon as counter electrode. Its V_{oc} is 0.44 V, close to the traditional flat cells, but I_{sc} is as low as 26 nA/cm^2, possibly because the TiO_2 thin film prepared by atomic layer deposition (ALD) is too dense, so it weakens the adsorption of dye molecules, thus weakens the ability of the cell to harvest light.

ZnO, due to its wider energy gap and its conduction band position similar to TiO_2, also has been widely used to prepare the DSSC photovoltaic electrode. Wang and co-workers [74] prepared ITO (300 nm)/ZnO (50 nm) thin layer by the radio frequency magnetron sputtering on the surface of optical fiber, and further fabricated their flexible fiber-shaped solar cell using vertical-growth ZnO as the photoanode whose structure is shown in Fig. 10A. The light is injected by irradiating internally from the fiber end. The power conversion efficiency is significantly increased due to continuously refractions and reflections many times inside the fiber. After the shape of optical fiber changed from cylindrical to rectangular, further by designing the rectangular optical fiber with ZnO grown on three sides of it, and the last side for its transparent electrode, which increases the light absorption (Fig. 10B). Moreover, after the contacting surface of the platinum counter electrode is changed from the original cylinder to the flat, its capacity of collecting and transmitting electric charge improves, the device's maximum efficiency can reach 3.3%, the highest efficiency reported currently on the ZnO-based fiber cells.

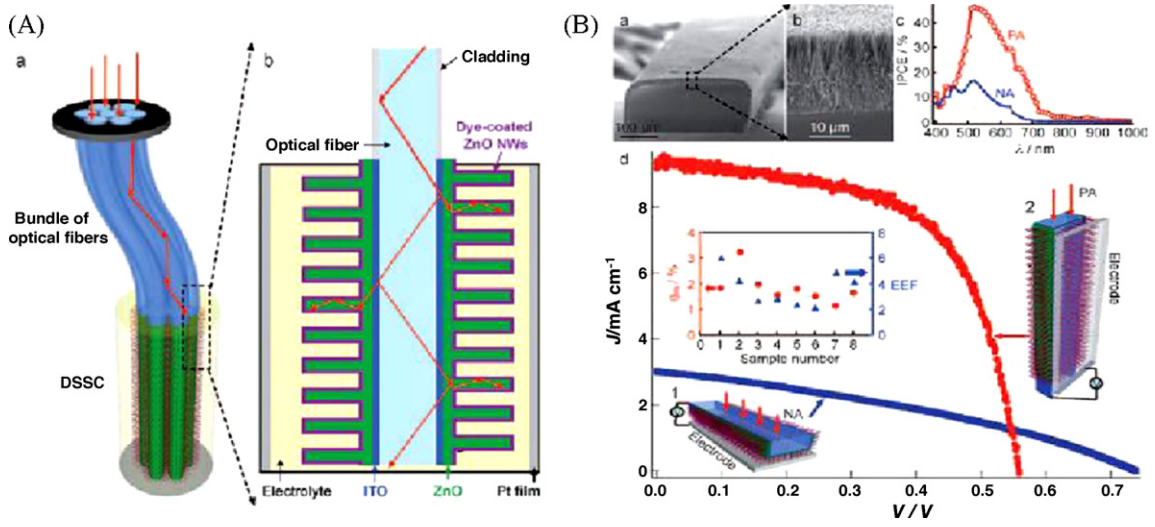

Fig. 10. (A) Design and principle of a three-dimensional DSSC. (B) Rectangular optical-fiber-based 3D DSSC and its performance.
Reproduced from Ref. [74].

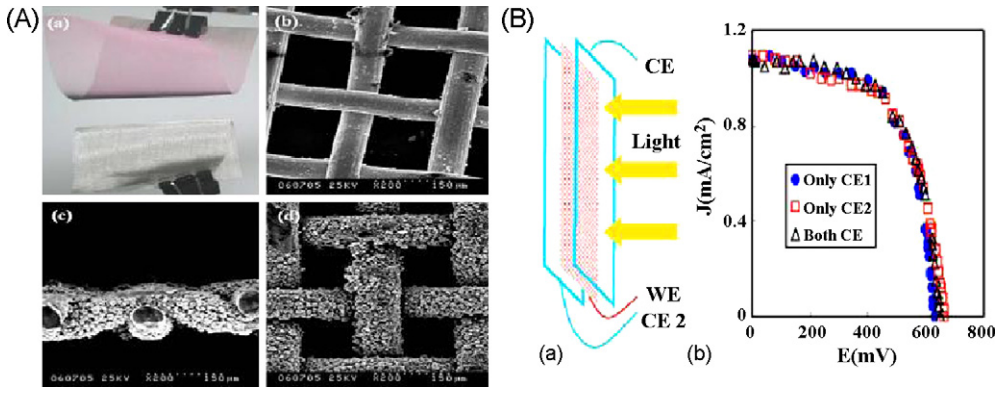

Fig. 11. (A) (a) Optical photo of the electrode (upper, 4.5 cm × 7 cm) and the net substrate (lower, 4 cm × 5.5 cm); (b) SEM photos of the mesh substrate; (c) and (d) top and sectional views of the as-prepared electrode. (B) (a) Structure of solar cells; (b) *I–V* performance.
Reproduced from Ref. [76].

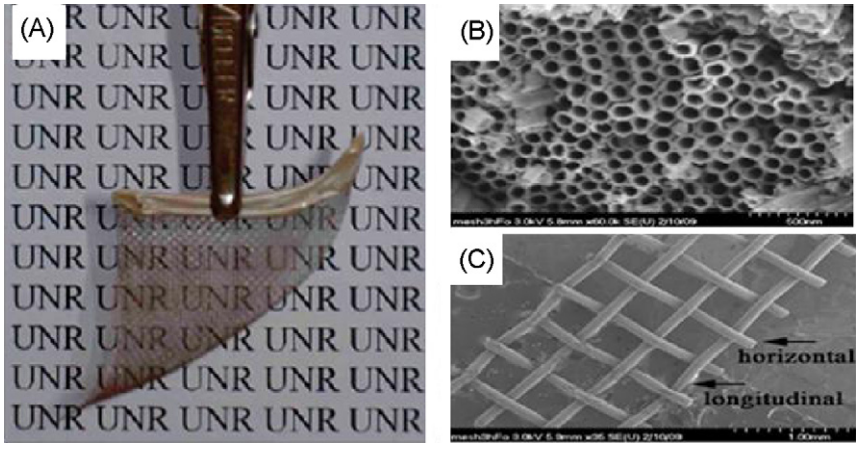

Fig. 12. (A) Triangular configuration of a Ti mesh after folding along the diagonal and its connection to a conductive clip via conductive silver paste; (B) Magnified top view of TiO_2 nanotube arrays on horizontal Ti wire; (C) Low-magnified overall image of the anodized mesh.
Reproduced from Ref. [77].

2.2.3. Other materials as photoanode substrates

It is necessary to develop new photoelectrode materials for flexible solar cells. Using the carbon fiber as the photoeletrode substrate, Unalan et al. [75] manufactured their cell with ZnO as its functional layer deposited by way of CVD on the carbon fiber, platinum as its counter electrode. The photoanode was sensitized by using "black dye", combined with a suitable electrolyte. The operation parameters of this solar cell, V_{oc}, J_{sc} and the fill factor are 350 mV, 11.2 mA/cm^2, and 0.28, respectively.

3. From the fiber-shaped to mesh-like solar cells

After fiber-shaped solar cells develop to a certain degree, in order to apply them in everyday life and industry, it is necessary to develop weaved cells with large area instead of the single cell mentioned above. The mesh-like structure can reduce the light loss by scattering to a minimum, and by combining fiber cells with different absorption bands, the cell module with whole absorption band can be realized, of all these advantages traditional cells do not possess themselves.

Zou's research group also studied the mesh-like cells [76]. By means of the preparation method similar to fiber-shaped cells, they manufactured the liquid dye-sensitized solar cell with 120-mesh stainless mesh coated the TiO_2 thin-film as its photoelectrode. The working electrode has very good flexibility, mechanical strength, and thermal stability. In this cell structure, shown in Fig. 11, light incidents from the working electrode side in which there are no restrictions of the electrode material on light transmittance, and the non-planar structure provides the center of scattering and diffuse reflection for the incident light, which not only improves the light harvesting of working electrode, but also reduces the dependence of incident light on the incident angle, all these are helpful for increasing the daily average photoelectric conversion rate. The performance of the solar cell is as follows: V_{oc} = 650 mV, I_{sc} = 4.5 mA/cm^2 and $\eta_{AM1.5}$ = 1.49% (100 mW/cm^2).

Misra and co-workers [77] further improved the preparation method for the working electrode. They fabricated the TiO_2 nanotube electrode on the Ti net through anode oxidation, the electrode has good light transmittance and strong fold-resistance which can be seen from Fig. 12. Using the TiO_2 nanotube electrode as its working one, the efficiency of this flexible dye-sensitized solar cell is up to 1.23%.

4. Summary and perspective

For flexible solar cells, not only their active layers (for example, for silicon-based solar cells and compound semiconductor-based solar cells), but also their substrates should meet the flexible requirement. Flexibility of substrate is directly and closely related to their power conversion efficiency, stability, cost, etc. One of the most important issues in research and development on flexible solar cells is to prepare such substrates characteristic of low

cost, high flexibility, high conductivity, high transparency, and high thermostability. Fiber-shaped solar cells broke limitations of the traditional flexible solar cells in shapes and materials, applied materials such as metal, optical fiber, conductive fiber, etc. to fabricate low cost and flexible photoelectrodes. The non-flat form of fiber substrates, on the one hand, increased absorption of scattered and reflected light, on the other hand, greatly expanded adaptability of solar cells to environment.

What is very worthy of attention is the transparent electrode-free (ITO-free) photovoltaic cell born in recent years. Because it does not need a transparent electrode, it overcomes many issues encountered in dealing with the transparent electrodes such as electrode material constraints, complex fabrication processes, high costs, and light, heat, and mechanical stabilities. Of course, compared with traditional plate cells, the efficiency of the current fiber cell is relatively low, the preparation process of its active layer needs to be improved, and efficiencies of light absorption, and charge transfer and collection need to be further increased. One can believe that with the in-depth study, fiber-shaped solar cells will show greater advantages in applications.

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References

[1] T. Yasufumi, Y. Yukihiro, T. Mikio, B. Toshiaki, K. Toshihiro, K. Hiroshi, S. Hitoshi, M. Eiji, T. Makoto, Sol. Energy Mater. Sol. Cells 93 (2009) 670.
[2] S. Wanger, J.L. Shay, P. Migliorateo, Appl. Phys. Lett. 25 (1974) 434.
[3] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, R. Noufi, Prog. Photovolt. 16 (2008) 235.
[4] P. Liska, N. Vlachopoulos, M.K. Nazeeruddin, P. Comte, M. Gratzel, J. Am. Chem. Soc. 110 (1988) 3686.
[5] B. O'Regan, M. Gratzel, Nature 353 (1991) 737.
[6] M.K. Nazeeruddin, A. Kay, I. Rodicio, R.H. Barer, E. Muller, P. Liska, N. Vlachopoulos, M. Gratzel, J. Am. Chem. Soc. 115 (1993) 6382.
[7] M. Gratzel, Prog. Photovolt.: Res. Appl. 8 (1) (2000) 171.
[8] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L.Y. Han, Japan. J. Appl. Phys. 2 (45) (2006) L638.
[9] S. Günes, H. Neugebauer, N.S. Sariciftci, Chem. Rev. 107 (4) (2007) 1324.
[10] H. Hoppe, N.S. Sariciftci, Adv. Polym. Sci. 214 (2008) 1.
[11] L.M. Chen, Z.R. Hong, G. Li, Y. Yang, Adv. Mater. 21 (2009) 1434.
[12] H.Y. Chen, J.H. Hou, S.Q. Zhang, Y.Y. Liang, G.W. Yang, Y. Yang, L.P. Yu, Y. Wu, G. Li, Nat. Photon. 3 (2009) 649.
[13] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (5243) (1995) 1789.
[14] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, Nature 376 (6540) (1995) 498.
[15] J. Boucleï, P. Ravirajan, J. Nelson, J. Mater. Chem. 17 (2007) 3141.
[16] M. JØrgensen, K. Norrman, F.C. Krebs, Sol. Energy Mater. Sol. Cells 92 (2008) 686.
[17] M. Helgesen, R. Søndergaard, F.C. Krebs, J. Mater. Chem. 20 (2010) 36.
[18] G. Dennler, M.C. Scharber, C.J. Brabec, Adv. Mater. 21 (2009) 1323.
[19] R.L. Crabb, F.C. Treble, Nature 25 (1967) 1223.
[20] T. Matsuyamat, K. Wakisaka, M. Kameda, M. Tanaka, T. Matsuoka, S. Tsuda, S. Nakano, Y. Kishi, Y. Kuwano, Jpn. J. Appl. Phys. Part 1: Regul. Papers Short Notes Rev. Papers 29 (1990) 2327.
[21] D.L. Staebler, C.R. Wronski, Appl. Phys. Lett. 31 (1977) 292.
[22] (a) P. Mario, P. Giovanni, L.B. Eric, C. Rosaria, I.M. Laura, F. Alexandra, J. Nanomater. (2008) 964046;
(b) B.J. Yan, G.Z. Yue, J. Yang, A. Banerjee, S. Guha, Mater. Res. Soc. Symp. Proc., vol. 762, 2003, p. 309.
[23] J. Yang, A. Banerjee, S. Guha, Appl. Phys. Lett. 70 (1997) 2975.
[24] (a) T. Soderstrom, F.J. Haug, V. Terrazzoni-Daudrix, C. Ballif, J. Appl. Phys. 103 (2008) 114509;
(b) H.B. Li, C.H.M. Vander Werf, A. Borreman, J.K. Rath, E.I. Schropp, Ruud, Phys. Stat. Solid I-Rapid Res. Lett. 2 (2008) 157;
(c) A. Vijh, X. Yang, W. Du, X. Deng, Sol. Energy Mater. Sol. Cells 90 (2006) 2657.
[25] D.H. Kim, J.H. Ahn, W.M. Choi, H.S. Kim, T.H. Kim, J.Z. Song, Y. Gang, Y. Huang, Z.J. Liu, C.L.J.A. Rogers, Science 320 (2008) 507.
[26] Z.Y. Fan, A. Javey, Nat. Mater. 7 (2008) 835.
[27] (a) A.N. Tiwari, M. Krejci, F.J. Haug, H. Zogg, Prog. Photovolt. 7 (1999) 393;
(b) N.G. Dhere, S.R. Ghongadi, M.B. Pandit, A.H. Jahagirdar, D. Scheiman, Prog. Photovolt. 10 (2002) 407;
(c) K. Herz, E. Kessler, R. Wachter, M. Powalla, J. Schneider, A. Schulz, U. Schumacher, Thin solid films 403 (2002) 384;
(d) F. Kessler, D. Rudmann, Solar Energy 77 (2004) 685;
(e) D. Rudmann, D. Bremaud, H. Zogg, A.N. Tiwari, J. Appl. Phys. 97 (2005) 084903;
(f) R. Birkmire, E. Eser, S. Fields, W. Shafarman, Prog. Photovolt. 13 (2005) 141;
(g) D. Bremaud, D. Rudmann, G. Bilger, H. Zogg, A.N. Tiwari, IEEE Photovolt. Specialists Conf. (2005) 223;
(h) D. Bremaud, D. Rudmann, M. Kaelin, K. Emits, G. Bilger, M. Doebeli, H. Zogg, A.N. Tiwari, Thin Solid Films 515 (2007) 5857;
(i) R. Birkmire, E. Eser, S. Fields, W. Shafarman, Prog. Photovolt. 13 (2005) 141;
(j) I. Shogo, H. Hiroyaki, K. Nobuaki, H. Kimikazu, Y. Akimara, N. Shigeru, Appl. Phys. Exp. 1 (2008) 092303;
(k) L. Zhang, Q. He, W.L. Jiang, F.F. Liu, C.J. Li, Y. Sun, Chin. Phys. Lett. 25 (2008) 3452;
(l) I. Shogo, Y. Akimasa, M. Koji, F. Paul, S. Keiichiro, N. Shigeru, Appl. Phys. Lett. 93 (2008) 124105.
[28] Y.S. Hsiao, C.P. Chen, C.H. Chao, W.T. Whang, Org. Electron. 10 (2009) 551.
[29] F.C. Krebs, Sol. Energy Mater. Sol. Cells 93 (2009) 394.
[30] F.C. Krebs, S.A. Gevorgyan, J. Alstrup, J. Mater. Chem. 19 (2009) 5442.
[31] F.C. Krebs, Org. Electron. 10 (2009) 761.
[32] F.C. Krebs, Sol. Energy Mater. Sol. Cells 93 (2009) 1636.
[33] B. Zimmermann, M. Glatthaar, M. Niggemann, M.K. Riede, A. Hinsch, A. Gombert, Sol. Energy Mater. Sol. Cells 91 (2007) 374.
[34] F.C. Krebs, M. Jørgensen, K. Norrman, O. Hagemann, J. Alstrup, T.D. Nielsen, J. Fyenbo, K. Larsen b, J. Kristensen, Sol. Energy Mater. Sol. Cells 93 (2009) 422.
[35] F.C. Krebs, Sol. Energy Mater. Sol. Cells 93 (2009) 465.
[36] F.C. Krebs, S.A. Gevorgyan, B. Gholamkhass, S. Holdcroft, C. Schlenker, M.E. Thompson, B.C. Thompson, D. Olson, D.S. Ginley, S.E. Shaheen, H.N. Alshareef, J.W. Murphy, W.J. Youngblood, N.C. Heston, J.R. Reynolds, S.J. Jia, D. Laird, S.M. Tuladhar, J.G.A. Dane, P. Atienzar, J. Nelson, J.M. Kroonl, M.M. Wienk, R.A.J. Janssen, K. Tvingstedt, F.L. Zhang, M. Andersson, O. Inganäs, M. Lira-Cantu, R. Bettignies, S. Guillerez, T. Aernouts, D. Cheyns, L. Lutsen, B. Zimmermann, U. Würfel, M. Niggemann, H.F. Schleiermacher, P. Liska, M. Grätzel, P. Lianos, E.A. Katz, W. Lohwasser, B. Jannon, Sol. Energy Mater. Sol. Cells 93 (2009) 1968.
[37] F.C. Krebs, M. Biancardo, B.W. Jensen, H. Spanggard, J. Alstrup, Sol. Energy Mater. Sol. Cells 90 (2006) 1058.
[38] C.J. Brabec, F. Padinger, J.C. Hummelen, R.A.J. Janssen, N.S. Sariciftci, Synth. Met. 102 (1999) 861.
[39] F.L. Zhang, M. Johansson, M.R. Andersson, J.C. Hummelen, O. Inganas, Adv. Mater. 14 (9) (2002) 662.
[40] T. Aernouts, P. Vanlaeke, W. Geens, J. Poortmans, P. Heremans, S. Borghs, R. Mertensa, R. Andriessen, L. Leenders, Thin Solid Films 451 (2004) 22.
[41] M. Al-Ibrahim, O. Ambacher, S. Sensfuss, G. Gobsch, Appl. Phys. Lett. 86 (2005) 201120.
[42] M.W. Rowell, M.A. Topinka, M.D. McGehee, H.J. Prall, G. Dennler, N.S. Sariciftci, L.B. Hu, G. Gruner, Appl. Phys. Lett. 88 (2006) 233506.
[43] A.K. Pandey, J.M. Nunzi, Appl. Phys. Lett. 89 (2006) 213506.
[44] J. Huang, X. Wang, Y. Kim, A.J. deMello, D.D.C. Bradley, J.C. deMello, Phys. Chem. Chem. Phys. 8 (2006) 3904.
[45] S.I. Na, S.S. Kim, J. Jo, D.Y. Kim, Adv. Mater 20 (2008) 4061.
[46] Y.S. Hsiao, C.P. Chen, C.H. Chao, W.T. Whang, Org. Electron 10 (2009) 551.
[47] J.A. Hauch, P. Schilinsky, S.A. Choulis, R. Childers, M. Biele, C.J. Brabec, Sol. Energy Mater. Sol. Cells 92 (2008) 727.
[48] H. Lindström, A. Holmberg, E. Magnusson, S.E. Lindquist, L. Malmqvist, A. Hagfeldt, Nano Lett. 1 (2) (2001) 97.
[49] G. Boschloo, H. Lindström, E. Magnusson, A. Holmberg, A. Hagfeldt, J. Photochem. Photobiol. A 148 (2002) 11.
[50] T. Yamaguchi, N. Tobe, D. Matsumoto, H. Arakawa, Chem. Commun. (2007) 4767.
[51] H. Lindström, A. Holmberg, E. Magnusson, L. Malmqvist, A. Hagfeldt, J. Photochem. Photobiol. A 145 (2001) 107.
[52] F. Pichot, J.R. Pitts, B.A. Gregg, Langmuir 16 (2000) 5626.
[53] A.D. Pasquier, Electrochimi. Acta 52 (2007) 7469.
[54] K. Kim, G.W. Lee, K. Yoo, D.Y. Kim, J.K. Kim, N.G. Park, J. Photochem. Photobiol. A 204 (2009) 144.
[55] D.G. Tauste, I. Zumeta, E. Vigil, M.A.H. Fenollosa, X. Domènech, J.A. Ayllón, J. Photochem. Photobiol. A 175 (2005) 165.
[56] C. Longo, J. Freitas, M.A.D. Paoli, J. Photochem. Photobiol. A 159 (2003) 33.
[57] D.S. Zhang, T. Yoshida, T. Oekermann, K. Furuta, H. Minoura, Adv. Funct. Mater. 16 (2006) 1228.
[58] S. Uchida, M. Tomiha, N. Masaki, A. Miyazawa, H. Takizaw, Sol. Energy Mater. Sol. Cells 81 (2004) 135.
[59] S. Ito, N.-L.C. Ha, G. Rothenberger, P. Liska, P. Comte, S.M. Zakeeruddin, P. Péchy, M.K. Nazeeruddin, M. Grätzel, Chem. Commun. (2006) 4004.
[60] Y. Jun, M.G. Kang, J. Electrochem. Soc. 154 (1) (2007) B68.
[61] D. Kuang, J. Brillet, P. Chen, M. Takata, S. Uchida, H. Miura, K. Sumioka, S.M. Zakeeruddin, M. Grätzel, ACS NANO 2 (6) (2008) 1113.
[62] B. Liu, J.E. Boercker, E.S. Aydil, Nanotechnology 19 (2008) 505604.
[63] W.W. Tan, X. Yin, X.W. Zhou, J.B. Zhang, X.R. Xiao, Y. Lin, Electrochim. Acta 54 (2009) 4467.
[64] Y. Jun, J. Kim, M.G. Kang, Sol. Energy Mater. Sol. Cells 91 (2007) 779.
[65] M.G. Kang, N.G. Park, K.S. Ryu, S.H. Chang, K.J. Kim, Sol. Energy Mater. Sol. Cells 90 (2006) 574.
[66] J.H. Park, Y. Jun, H.G. Yun, S.Y. Lee, M.G. Kang, J. Electrochem. Soc. 155 (7) (2008) F145.

[67] B. O'Connor, K.P. Pipe, M. Shtein, Appl. Phys. Lett. 92 (2008) 193306.
[68] M.R. Lee, R.D. Eckert, K. Forberich, G. Dennler, C.J. Brabec, R.A. Gaudiana, Science 324 (2009) 232.
[69] X. Fan, Z.Z. Chu, F.Z. Wang, C. Zhang, L. Chen, Y.W. Tang, D.C. Zou, Adv. Mater. 20 (2008) 592.
[70] X. Fan, Z.Z. Chu, L. Chen, C. Zhang, F.Z. Wang, Y.W. Tang, J.L. Sun, D.C. Zou, Appl. Phys. Lett. 92 (2008) 113510.
[71] H. Wang, Y. Liu, M. Li, H. Huang, M.Y. Zhong, H. Shen, Appl. Phys. A 97 (2009) 25.
[72] H. Wang, Y. Liu a, H. Huang, M.Y. Zhong, H. Shen, Y.H. Wang, H.X. Yang, Appl. Surf. Sci. 255 (2009) 9020.
[73] M. Toivola, M. Ferenets, P. Lund, A. Harlin, Thin Solid Films 517 (2009) 2799.
[74] B. Weintraub, Y.G. Wei, Z.L. Wang, Angew. Chem. Int. Ed. 48 (2009) 8981.
[75] H.E. Unalan, D. Wei, K. Suzuki, S. Dalal, P. Hiralal, H. Matsumoto, S. Imaizumi, M. Minagawa, A. Tanioka, A.J. Flewitt, W.I. Milne, G.A.J. Amaratunga, Appl. Phys. Lett. 93 (2008) 133116.
[76] X. Fan, F.Z. Wang, Z.Z. Chu, L. Chen, C. Zhang, D.C. Zou, Appl. Phys. Lett. 90 (2007) 073501.
[77] Z.Y. Liu, V. Subramania, M. Misra, J. Phys. Chem. C 113 (2009) 14028.