

REVIEW

Fabrication of flexible dye sensitized solar cells on plastic substrates



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Abstract

This article introduces the latest progress in the research on fabrication of flexible dye-sensitized solar cells (DSSCs), in particular the choice of flexible plastic substrates replacing the conventionally used rigid glass substrates. A major challenge for making DSSCs on plastic substrates is the temperature limitation of the substrate in producing the TiO₂ working electrode. Several low-temperature fabrication methods for nano-porous TiO₂ films, such as ball-milling, acid/water treatments, chemical vapor deposition and electrophoretic deposition, as well as recently studied chemical and mechanical film processing methods such as chemical sintering, hydrothermal treatment, microwave irradiation, and different compression techniques are extensively discussed here. It also presents studies on new fabrication methods of flexible counter electrodes and recently developed new materials particularly useful for flexible DSSCs. At last, the developments and prospects of fabricating large scale flexible DSSC modules and their durability are discussed.

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Introduction

Photovoltaic (PV) technology has been realized as a suitable renewable power source for the fulfilment of increasing world energy consumption with least impact on the environment. In the last two decades there has been a growing interest for fabrication of low-cost solar cells based on molecular materials and semiconductor nano-structures. Silicon based solar

cells dominate the commercial market at the present time, but their manufacturing involves energy intensive processes and high vacuum conditions, which lead to high manufacturing costs. In this regard, dye sensitized solar cells (DSSCs) [1,2] and organic solar cells (OSCs) [3–5] have demonstrated their potentials as relatively low-cost alternatives to silicon solar cells. An attractive advantage of OSCs is the potential for roll-to-roll printing on polymer substrates. The absence of a liquid electrolyte also makes processing and sealing of OSC devices comparatively simpler. However, electrochemical solar cells using TiO₂ electrodes, in combination with Ru-based dyes and iodine-based liquid electrolyte are on the verge of entering the

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photovoltaic market due to its superior power conversion efficiency (PCE) over the organic solar cells and relatively low production cost. Efficiencies over 12.5% have already been achieved for the lab size devices [6] and over 8% efficiency has been recently reported for devices using a p-type compound ($\text{CsSnI}_{3-x}\text{F}_x$) as a solid state electrolyte [7].

Lately, there has been an increased demand for lightweight, flexible electronic devices as they can be produced in large scales using printing techniques at room temperature with a much reduced production cost. The concept of flexible polymer based solar cells has thus attracted much interest amongst researchers in the field of DSSCs. However there are many unanswered issues related to the fabrication of flexible DSSCs. In this article, the technological development of DSSCs on flexible substrates is reviewed, with a focus on polymer substrates and the factors related to the slurry preparation, deposition of films and processing of electrodes to improve the mechanical and photovoltaic properties of the device.

Structure and working principle of DSSCs

The structure of a dye sensitized solar cell mainly consists of three major components, namely: the working electrode which is usually a dye molecule coated nanocrystalline porous TiO_2 film deposited on a transparent conductive oxide (TCO) coated substrate, the counter electrode which is often a platinum-coated TCO deposited substrate and an electrolyte containing usually an I^-/I_3^- redox couple. Figure 1(A) illustrates the components in a typical DSSC. In the $\sim 10\ \mu\text{m}$ thick mesoporous working electrode, TiO_2 particles are bonded to each other and to the TCO glass substrate by sintering at $450\text{--}550\ ^\circ\text{C}$. Additionally, the mesoporous structure of the TiO_2 film provides a large surface area to accommodate a high amount of dye molecules which enhances the amount of light absorption [8]. A variety of nano crystalline semiconductor particles (mainly TiO_2) can be prepared by the sol-gel technique. The TiO_2 film is usually deposited on a TCO coated glass substrate using TiO_2 slurry containing various solvents and organic binders. The binders in the TiO_2 slurry reduce the stresses of the film during drying, and assist in the formation of well-adhered titania layers on the TCO glass substrates. These electrodes are then sintered at $450\text{--}550\ ^\circ\text{C}$ to remove the binders in the film, as well as to form chemical bonding between TiO_2 particles and the TiO_2 particles with the TCO layer on the substrate via a solid state diffusion mechanism. Sintered electrodes are soaked in a dye solution to allow for the dye adsorption, and then sandwiched with a platinum-coated counter electrode. The Pt coating is usually prepared either by thermal decomposition or by sputtering techniques. The voids between TiO_2 particles and the space between the TiO_2 layer and the counter electrode are filled with a liquid electrolyte containing I^- and I_3^- redox couple. Generally, these types of solar cells are exposed to the solar radiation from the working electrode side of the TCO glass, known as front illumination (Figure 1(A)).

The working principle of the DSSC is based on the absorption of photons and excitation of the dye, followed by fast electron injection into the conduction band (CB) of

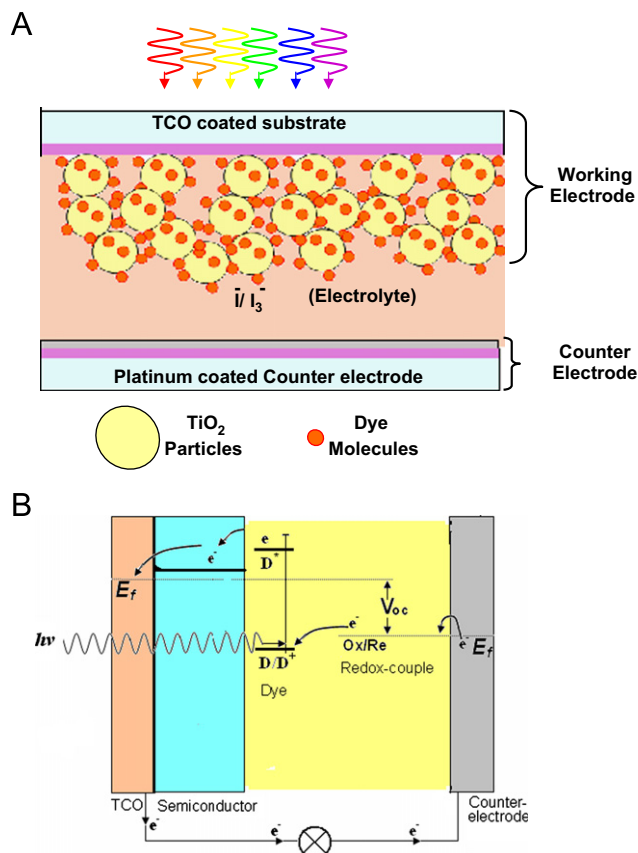


Figure 1 (A) Structure and (B) principle of a dye sensitized solar cell.

the TiO_2 surface. Figure 1(B) shows the operation principle of the DSSC. Dye molecules absorb the incident photons and get excited from a low-energy state (HOMO-highest occupied molecular orbital) to a high-energy state (LUMO-lowest unoccupied molecular orbital). The excited state of the dye molecule is capable of injecting electrons into the CB of the TiO_2 particle. The oxidized dye is then regenerated and becomes ready for the next excitation by obtaining electrons from the redox electrolyte converting iodide (I^-) in to tri-iodide (I_3^-). The electrons injected to the CB of TiO_2 percolate through the TiO_2 particles in the film until they are collected at the TCO contact of the photoelectrode, and are fed in to the external circuit. The tri-iodide species (I_3^-) are converted back to iodide (I^-) via the platinum catalyst at the counter electrode by the electrons traveled through the external circuit.

Flexible DSSCs

Advantageous of flexible DSSCs

For any photovoltaic technology, flexible solar panels offer some advantages over classic rigid solar panels. When it comes to the installation, plastic substrate based PVs can be installed quickly on buildings with flat or curved surfaces because of the light weight and flexible nature of these

types of PVs. Therefore, although DSSCs fabricated on TCO coated glass have achieved efficiencies above 12%, there is a great deal of interests in cheaper, flexible solar cells using transparent indium tin oxide (ITO) coated plastic electrodes (usually polyethylene naphthalate (PEN) and polyethylene terephthalate (PET)) in place of the glass. Flexibility and light weight are two important advantages of using plastic substrates. Flexible solar cells would be adaptable to different shapes of surfaces and light weight would enable them as a mobile power source for portable electronic devices.

Flexible DSSCs are important not only for user convenience, but also for realizing roll-to-roll mass production. The cost of solar cells would be significantly reduced by this fast, continuous manufacturing process. TCO coated glass substrates account for a significant portion of the cost of the device. A replacement of polymer substrates for glass is expected to reduce the materials cost as well.

Challenges in flexible DSSCs

Deposition of TiO_2 nano crystalline films on plastic substrates for working electrodes has become a great challenge, as most plastic substrates limit the thermal treatment to around 150°C . This precludes using any organic binders during the film deposition, as they would normally remain in the TiO_2 film processed below 400°C . Absence of binders in TiO_2 pastes would result in the formation of cracks in the film during drying and thus increase electrical resistivity. Decreased adhesion of the TiO_2 film with the substrate and poor electrical contact between TiO_2 particles are the other difficulties when plastic substrates are used due to low temperature processing. Poor stability of the devices due to the ingress of moisture and oxygen through the highly permeable plastic substrates is a major problem faced by both DSSC and OSC technologies based on plastic substrates. Thus a rigorous encapsulation technology that has no significant effect on the production cost would be essential when commercializing these modules.

The working electrode of a DSSC consists of a porous TiO_2 film of $\sim 10\ \mu\text{m}$ thickness. When electrons are injected from the dye molecules into TiO_2 particles, they must travel through a large number of titania nanoparticles (10^6 and 10^7) in order to reach the TCO layer [9]. In glass-based DSSCs, the inter-particle chemical connection (so called necking) and strong connectivity of the titania layer with the substrate are achieved by the high temperature sintering process, which are essential for achieving high efficiency DSSCs. Furthermore, due to lack of binders, the TiO_2 slurries used for casting films often have difficulties to wet hydrophobic polymer substrates, resulting in poor adhesion with the substrates [10]. The restriction of high temperature heat treatments is a major factor responsible for the relatively low conversion efficiency of plastic based DSSCs. Thus, some modifications are required in the preparation of TiO_2 pastes and alternative techniques have to be employed to improve the bonding between TiO_2 particles and the TiO_2 film with the substrate for the fabrication of DSSCs on plastics with improved efficiencies.

Preparation of TiO_2 pastes for flexible DSSCs

Preparation of suitable TiO_2 pastes with appropriate rheology to produce high quality mechanically stable films without organic binders is the first major challenge facing when fabricating DSSCs on plastic substrates. In order to prevent film cracks due to the large agglomerates, the TiO_2 nanoparticles are required to be well dispersed in the paste. Our work showed the importance of the ball-milling technique for the preparation of well dispersed TiO_2 slurries using relatively cheap Degussa P25 TiO_2 powder as the raw material [11]. De-agglomeration by such a milling led to an increase of the film strength and the surface area, improving dye adsorption in titania films. A maximum power conversion efficiency of 4.2% was achieved for the plastic based solar cells prepared using the ball milling technique. It is very important to evaluate the inter-particle bonding of the mesoporous nanocrystalline metal oxide films. However, currently there is no such method developed to measure the inter-particle bonding between metal oxide nano particles. Here, a method of nanoindentation was firstly developed for this purpose. A nano-scratch test was performed with the nanoindentation instrument to measure the force required for making a scratch, which has shown its potential as a more quantitative alternative to the conventional testing methods such as bending deformation [12,13], pencil scratch test [14-16] and measuring the resistance of the film for the ultra-sonication [17]. In a typical nanoscratch test, a stylus or a diamond tip is moved over the film surface. The test is performed by the combination of two types of tip movement with respect to the film surface in normal (vertical) and lateral (horizontal) motions. Forces exerted on the tip are monitored in normal and lateral directions while forming a scratch with known depth and length, and they are used to compare the film strength [11]. Using this technique, the mechanical strength of the mesoporous TiO_2 films was found to increase with longer milling time of the slurries, corresponding to some improvements in conversion efficiency of plastic based DSSC devices [11].

For printing processes, such as screen printing and gravure printing, pastes with high viscosity are required. However, commonly used water or alcohol based binder free titania slurries usually exhibit very low viscosity. Therefore investigation of the factors associated with the paste rheology and their influence on the inter-particle connectivity has been a key interest for fabricating flexible DSSCs. To date, only a few highly viscous pastes suitable for a single step coating process on ITO coated plastic substrates have been developed [18,19]. The rheological behavior of ethanol based titania pastes was investigated and it was found that with the addition of ammonia, hydrochloric acid and water, the viscosity of TiO_2 pastes could vigorously be changed (Figure 2) [20,21]. The change in the viscosity has been correlated with the measured zeta potential of the colloidal titania pastes. Improved inter-particle connectivity and hence better solar cell performance was achieved for the ethanol based pastes containing acid or water. Maximum light to electrical energy conversion efficiencies of 4.9% and 5.0% were obtained for the plastic based dye-sensitized solar cells fabricated using water and acid-added slurries, respectively. A similar study was reported by Park et al. [22] to prepare highly viscous

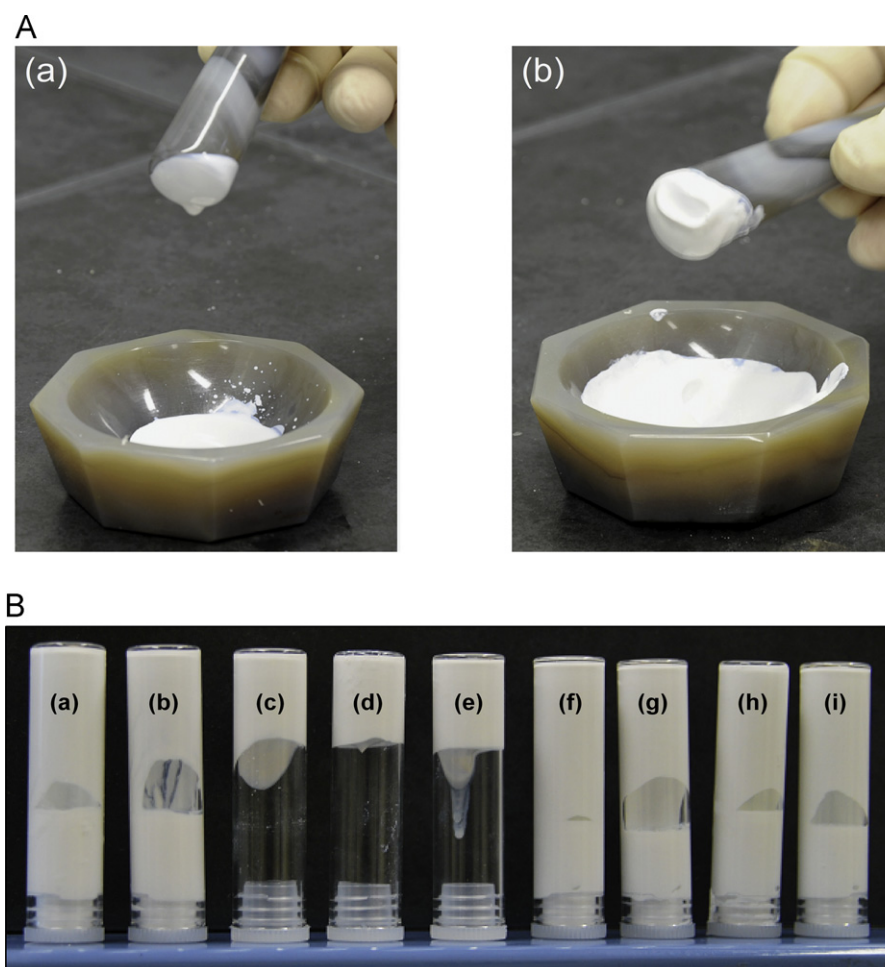


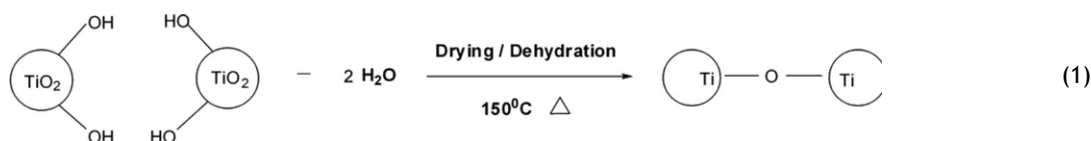
Figure 2 (A) Comparative images of change of viscosity for an ethanol based TiO_2 slurry (a) before and (b) after adding HCl (0.025 M). (B) Change in viscosity of an ethanol based titania paste (30 wt% solid loading) prepared with different water percentages. ((a)=0%, (b)=5%, (c)=10%, (d)=20%, (e)=30%, (f)=40%, (g)=60%, (h)=80% and (i)=100%) [20,21].

TiO_2 colloidal pastes by adding concentrated ammonia into acidic colloidal solutions.

Another method to increase the viscosity and the connectivity of TiO_2 particles is to mix of small amounts of Ti-monomers into TiO_2 pastes [17,23,24]. Normally, a hydrothermal treatment is carried on after the mixing of the Ti-monomers. During the drying process and the hydrothermal treatment, Ti-monomers could transfer into crystalline TiO_2 , forming firm chemical bonding between TiO_2 nanoparticles in the film. A study found hydrothermal treatments at (100 °C) achieved fairly high efficiencies (4.2%) for TiO_2 films prepared on FTO coated glass substrates [24]. But different results were observed when the low temperature hydrothermal treatment was used to make plastic based DSSCs. Zhang et al. [24] reported the use of three different pastes of P25 TiO_2 powder mixed with TiCl_4 , TiOSO_4 and Ti-tetraisopropoxide for low temperature TiO_2 electrode preparation. Only the Ti-tetraisopropoxide containing paste could be tested on ITO-PET substrates due to the high acidity of the other two pastes, damaging the ITO coating. The coated TiO_2 films were subjected to a hydrothermal treatment in a Teflon-lined autoclave at 100 °C for 12 h and the process only achieved a 2.5% efficient flexible

solar cell. The low efficiency was attributed to the increased resistance of the ITO layer due to the hydrothermal treatment. The other limitation of the process is that it is incompatible with continuous printing for large-scale manufacturing.

A recent result with a high efficiency (5.8%) for plastic DSSCs fabricated using a highly viscous TiO_2 paste (PECC-K01, Peccell Co. Ltd) was reported by Yujiro et al. at Toin University of Yokohama, Japan [25]. This paste was prepared by mixing various sizes of TiO_2 particles (10-150 nm) with a small amount of larger TiO_2 particles (250 nm) to enhance light scattering. In addition, an aqueous colloidal sol of 10-30 nm TiO_2 particles was used as an inter-particle connection agent. The effect of particle size on the cell efficiency was also studied. It was found that higher dye adsorption and photocurrent were obtained for an average particle size of 60 nm. It was assumed that the interparticular connection among TiO_2 particles was produced by the dehydration of hydrogen bonded network of TiO_2 nanoparticles, as shown in Equation (1). This process is also referred to as “chemical sintering” [26]. However, it is still unclear about the thickness and the crystalline nature of the inter-particle layer formed by such colloidal sols, which would be critical for the further improvement of the cell efficiency.



Preparation and processing of TiO₂ working electrodes for flexible DSSCs

Film preparation

Different low temperature coating and deposition techniques have been attempted and reported for the preparation of TiO₂ electrodes on flexible substrates. Generally the preparation of TiO₂ electrodes on plastic substrates has been carried out by casting a paste containing TiO₂ nanoparticles dispersed in solvents of a low boiling point using doctor blading technique. However, a number of other direct deposition methods, such as electrophoretic deposition [27–33], chemical vapor deposition (CVD) [34,35] spray deposition [36,37] and pulsed laser deposition (PLD) [38] techniques have been successfully employed for the preparation of TiO₂ electrodes on flexible substrates.

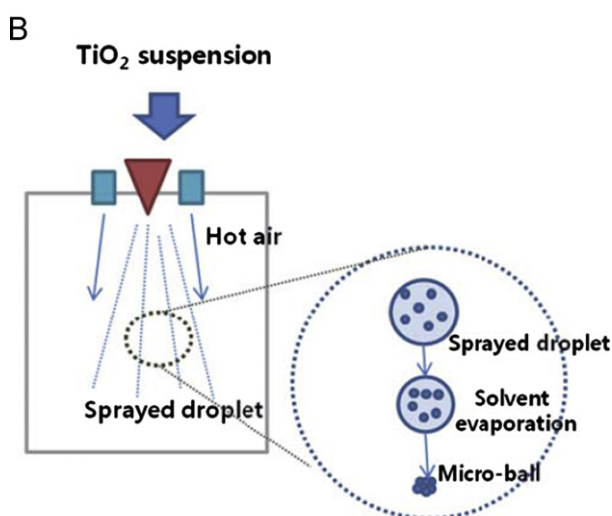
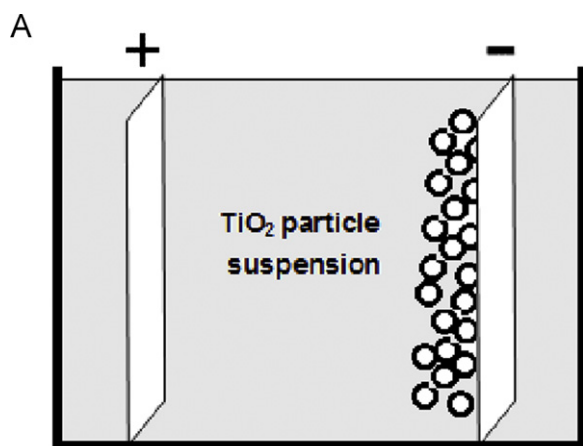


Figure 3 A schematic illustrations of (A) electrophoretic deposition and (B) spray-drying techniques [37].

Electrophoretic deposition is a material processing technique in which charged particles in a suspension are moved toward an oppositely charged electrode and are deposited onto a substrate under externally applied DC electric field (Figure 3(A)). It has advantages over other coating processes due to less complexity, controllability of the film thickness and ability to deposit films with preferred patterns irrelevant to the substrate shape. Power conversion efficiencies exceeding 6% have recently been reported by Grinis et al. [33] for the electrophoretically deposited mesoporous TiO₂ nanoparticles on plastic substrates. Spray deposition can be considered as another low cost and simple process to directly deposit thin nanoporous films with precise thickness using colloidal solutions. This technique can also be integrated into a continuous reel-to-reel deposition system. However some post-treatments are required to improve the inter-particle connectivity and the film/substrate adhesion to achieve comparatively high power conversion efficiencies for the spray deposited electrodes on flexible substrates. Cha et al. has attempted utilizing a dye spray technique to prepare pre-sintered TiO₂ micro-balls and achieved efficiencies just over 2% (Figure 3(B)), [37].

For the preparation of TiO₂ photoelectrode films, doctor blading has been widely used for the small scale preparation of TiO₂ films [11,20,21,39]. This method has not yet been proved as a suitable technique that can be applied in a large-scale roll-to-roll fabrication. Thus, screen printing, gravure/reversed gravure and spraying techniques have been considered as alternate methods for the continuous preparation of TiO₂ electrodes. Fabrication of DSSCs on flexible substrates totally relies on the development of large scale printability of mechanically stable thick TiO₂ films (5–15 μm) on the substrates. So far only few works has been reported on the large scale preparation of TiO₂ films for flexible DSSCs.

Film processing techniques

The printed TiO₂ films require an additional processing step to improve the necessary inter-particle contact for their effective performance as an electrode material, as well as to improve the mechanical stability, namely good film-substrate adhesion. Organic binders were used for making flexible DSSCs, but absence of high temperature sintering of the TiO₂ film on polymer substrates resulted in incomplete necking of the particles due to the presence of residual organics in the film. UV/ozone treatment of the deposited TiO₂ films was used by several groups as a method for eliminating adsorbed organic impurities on the surface of TiO₂ films (Figure 4) [40], but it only achieved a modest improvement in efficiency of the devices [41–43]. Moreover, the effect of UV radiation on improving the inter-particle connection was also investigated as another low temperature sintering method for flexible DSSCs [40,44].

Some alternative sintering techniques have been attempted to improve the necking of TiO₂ nanoparticles without damaging

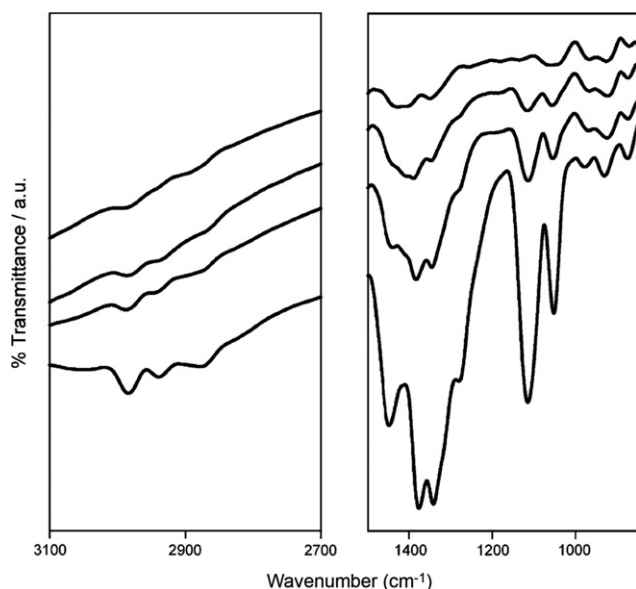


Figure 4 ATR-FTIR spectra of the TiO_2 film after different times of irradiations (From bottom to top: 0, 1, 2, and 6 h) indicating that most of the organic substances are eliminated after the UV treatment [40].

the plastic substrate. Microwave heating can be a selective heating process, depending on materials responses to the microwave radiation. For example, many polymers have low loss tangent and thus are transparent to microwave, while many oxides are good microwave absorbers. Uchida et al. heat-treated TiO_2 films on ITO/PET substrates in a microwave oven at 2.45 GHz and 28 GHz frequencies and achieved 0.74% and 2.2% conversion efficiency respectively [45]. The efficiency improvement by higher frequency heating was mainly resulted from a significant increase in the photocurrent of the DSSC device. However, more work is needed to verify if TiO_2 particle interconnection was improved in the microwave heating.

Mechanical compression is one of the widely used alternative techniques for making DSSCs on plastics and the technique can be compatible to a roll-to-roll production line [46–48]. In this technique, an external pressure is applied on the dried TiO_2 films deposited on polymer substrates in order to enhance the particle-particle and film-substrate connectivity. So far the highest efficiency for the polymer based DSSC is reported by the Arakawa group in Japan, using a uniaxial compression technique and modified TiO_2 pastes [47]. In their work, a compressive pressure was applied on the doctor bladed TiO_2 films using a uniaxial Mini Test Press (Toyo Seiki) and the maximum pressure applied on the films was limited to 100 MPa. Maximum efficiency and maximum photocurrent of 8.1% and 14.5 mA/cm^2 were reported in this work. However, it remains a challenge to achieve high uniformity in a $\sim 10 \mu\text{m}$ thick TiO_2 film by such a uniaxial pressing, especially when the TiO_2 film area is large, as it would require the two pressing plates to be perfectly parallel and to have mirror flat surfaces. On the other hand, a cold isostatic pressing (CIP) technique has been applied for the first time by Cheng's group to press TiO_2 films on plastic substrates for flexible DSSCs [39,49]. CIP is a powder compaction technology widely used in metallurgy

and ceramic industries to make strong green bodies of complex shapes. In the CIP process, the same pressure is applied through a liquid medium in all directions uniformly, independent of the size and the shape of the pressed material. High pressure can be applied through the CIP to very large size materials, being bulky pieces or thin films. Because the pressure is applied through a liquid medium, the technique has unique advantages for pressing thin films and non-flat solar cells. As observed in Figure 5, due to the deaggregation by CIP compression, the CIP-pressed films became more transparent and showed increased light transmittance with higher pressure [39]. Such increase in transparency of the electrodes can also be associated with the improved film uniformity and reduction of the film thickness due to the compression. Both normal and lateral forces measured by the nanoindentation scratch test on the CIPed TiO_2 films showed a significant increase with increasing the CIP pressure. Electrodes processed by the CIP method have yielded high conversion efficiencies of 6.3% and 7.4% for simulated sun lights of 100 and 15 mW cm^{-2} respectively, a marked improvement compared to that without the CIP pressing [46]. Although CIP is a batch process, it is a mature manufacturing technology. Large CIP facilities are commercially available for pressing a very large number of solar cell modules in one batch, thus can be compatible with commercial scale manufacturing.

When the low temperature prepared TiO_2 nanocrystalline film is compressed, the connection between the TiO_2 nanocrystals is not a chemical bonding but merely a physical contact. Thus, there are still barriers for the electron transport especially at high electron density. Normally the PCE of DSSCs is lower at high light intensity compared to that at low light intensity. In order to improve the PCE of the plastic DSSC, Dürr et al. developed a new method, permitting the use of slurries containing organic binders and high temperature sintering for flexible TiO_2 photoelectrodes [50]. This “lift off” technique is based on the formation of a sintered titania film on a glass substrate and then transferring it to a plastic substrate. Efficiency close to 6% was reported for the transferred electrode systems on plastic substrates. Initially nano crystalline TiO_2 films were screen printed on gold layer deposited glass substrates. Inter-particle connection of TiO_2 films was achieved by high temperature sintering. The sintered TiO_2 film was separated from the glass substrate by chemical dissolution of the gold layer and then transferred on to an ITO-PEN substrate as shown in Figure 6 [50]. Despite the high efficiency achieved, this is not a commercially viable technique due to high expenses and the complexity of transferring steps required during the process.

The mechanical compression methods, especially the CIP technique, can easily achieve mechanically stable TiO_2 films on plastic substrates. But the high temperature sintering does show the advantage on the electron transport compared with the compression processes. To combine the two techniques together, a new concept of “building blocks” has recently been developed by Cheng's group to construct high efficiency working electrodes on plastic substrates with a novel and facile approach [51]. The building blocks are the agglomeration units in which nanocrystalline TiO_2 particles are constructed in a mesoporous structure. By pre-treating the build blocks at high temperatures, it can induce strong

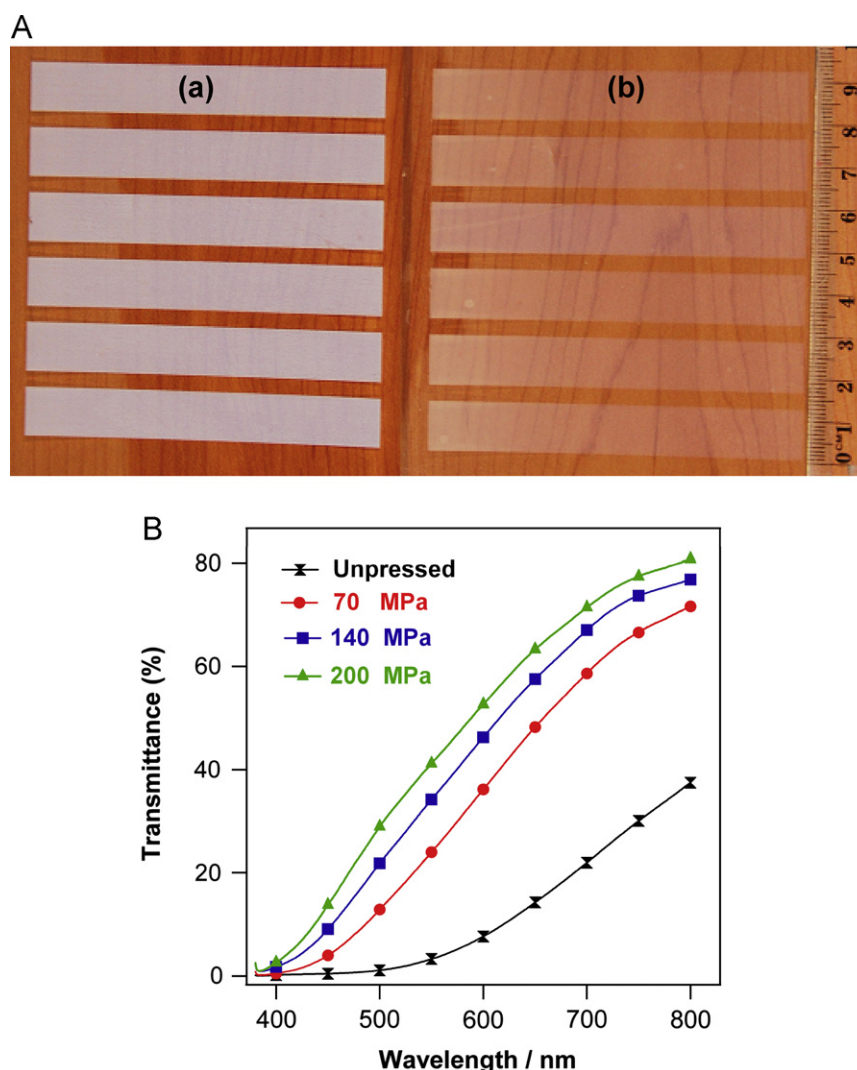


Figure 5 (A) Appearance of the TiO₂ electrodes (a) before and (b) after processed by CIP. (B) Variation of the transmittance of the TiO₂ films on ITO-PEN substrates processed at different CIP pressures. All the films had the same thickness (12 μ m) before CIP compression. [39].

chemical connections between the nanocrystals. These sintered building blocks can then be used to build the working electrode films on plastic substrates by a compression process. Submicrometer-sized mesoporous TiO₂ beads shown in Figure 7(a) [52] were employed as an example of building blocks to demonstrate the superiority of using such a processing strategy. The beads were synthesized via a combination of a sol-gel self-assembly process and a solvothermal process [53,54]. Such mesoporous titania beads have the following features: (1) high surface areas for effective adsorption of sensitizers, as a result of the presence of abundant and well-interconnected mesopores within the beads [54]; (2) strong light scattering capability due to the comparable beads size to the wavelength of the visible light [52] and (3) fast electron transportation via the densely-packed and chemically-bonded anatase network inside the beads [55] as clearly shown in Figure 7(b), [51]. The beads building blocks were compared with the powdered nanoparticles when constructed into working electrodes for flexible DSSCs by the CIP compression technique. Figure 7(c and d) [51] shows the schematic graphs of the

two types of electrodes. The building blocks could be pre-sintered at 500–650 $^{\circ}$ C, thus there would be comparable inter-particle necking for electron transport within the beads as that in the sintered nanoparticles. The main barrier comes from the relatively poor contact between the beads. The plastic DSSCs made from building blocks showed much higher PCE (6.6%) than that (4.9%) made from powdered nanoparticles (18 nm) [51]. Electrochemical Impedance Spectroscopy (EIS) studies clearly showed that the building block electrode had much faster electron diffusion rate (near 1 order of magnitude higher) than that in the powered nanoparticle electrode. Ke et al. also employed the similar TiO₂ beads structure to build the electrode, and found fast electron transport in the electrode [56]. Furthermore, the pre-sintered beads were treated with a 40 mM TiCl₄ solution, followed by a high temperature sintering to form core-shell structured TiO₂ beads, which was an essential step to increase the photocurrent involved in the glass substrate based DSSCs previously [57]. The treated building blocks were used to make films on plastic substrates via the CIP process. The

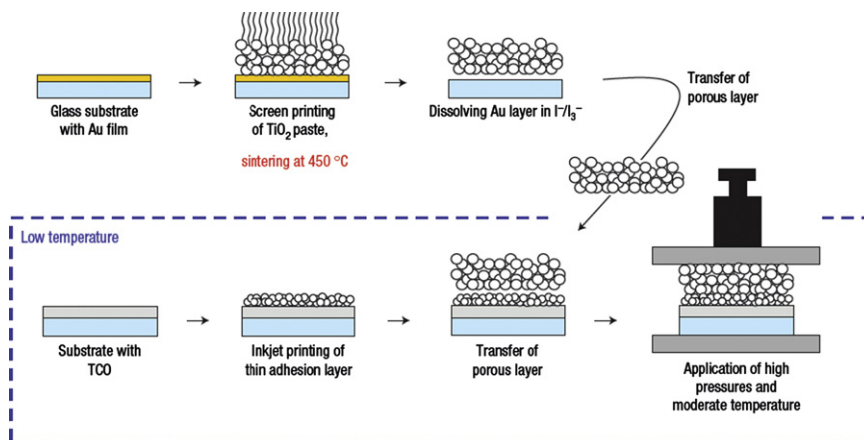


Figure 6 Individual steps of lift-off and transfer process [50].

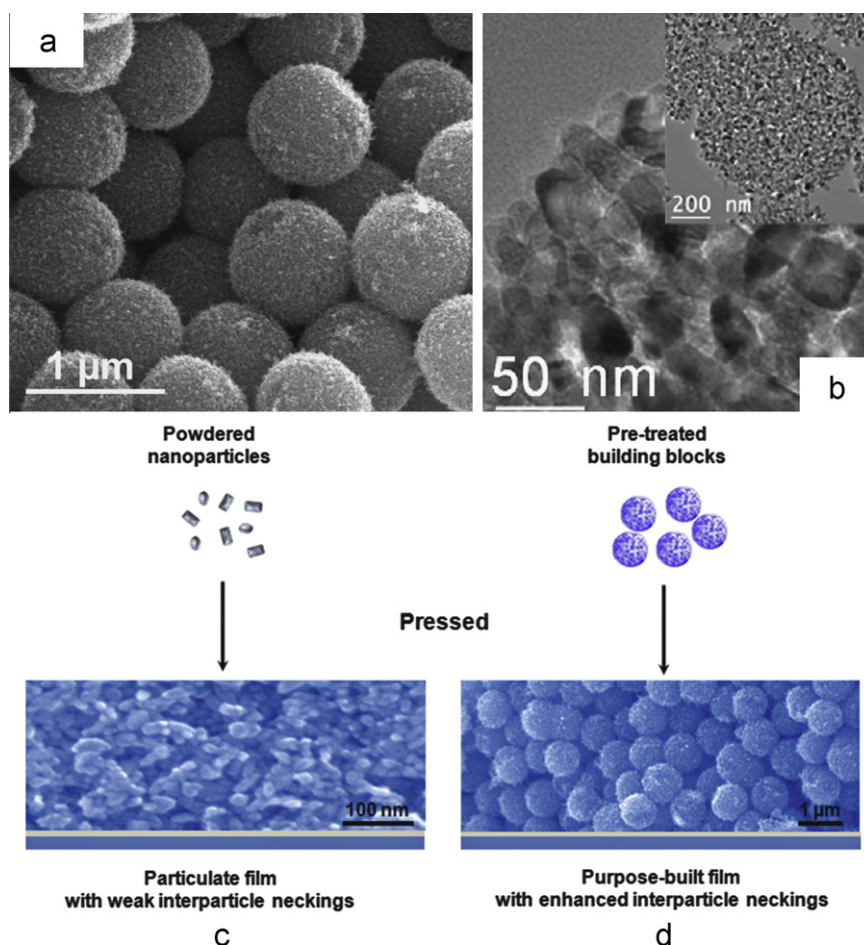


Figure 7 (a) SEM [52] and (b) TEM images of titania mesoporous beads, and schematic representation of titania films constructed from (c) powdered nanoparticles and (d) building blocks [51].

final PCE was greatly improved up to 7.5%, an efficiency rarely reported in the literature for plastic DSSCs. The improvement is attributed to the enhancement of the photocurrent due to the TiCl_4 treatment, from 13.18 mA/cm^2 to 15.41 mA/cm^2 [51].

Although the efficiency of flexible DSSCs has been gradually improved, it is still lower than that of glass substrate-based DSSCs. In order to further improve the performance

of flexible DSSCs, it is necessary to minimize the difference between processing of electrodes on flexible and glass substrates. The 1D structures provide a possible resolution. The 1D structures, such as ZnO nanowires and TiO_2 nanotubes can be directly grown on a substrate via a relatively low temperature processing condition [58,59]. Such 1D structures not only hold fast electron diffusion channels, but also provide the free space between nanorods/wires/

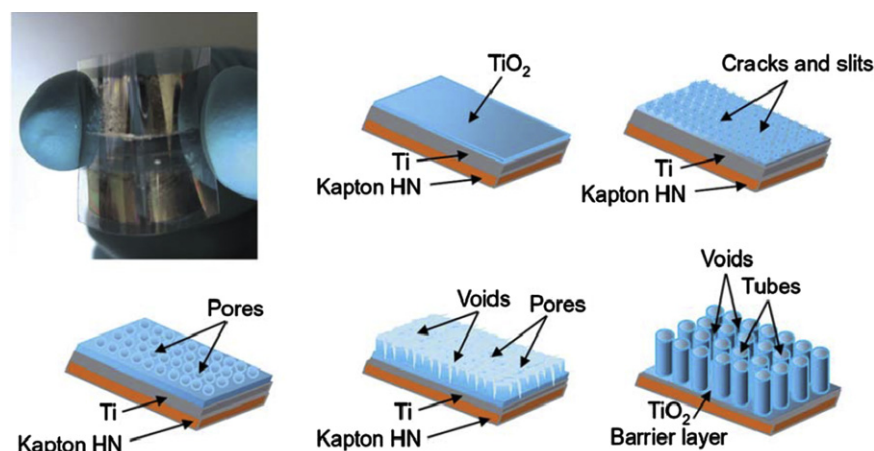


Figure 8 Picture of TiO_2 nanotubes grown over $10 \times 10 \text{ mm}^2$ areas on Kapton HN substrate and scheme of nanotube array formation [59].

tubes allowing for bending. Vomiero et al. anodized a titanium layer deposited on a PET/Kapton substrate by sputter coating to grow TiO_2 nanotubes for flexible devices, as shown in Figure 8 [59].

The Kapton substrate used in Figure 8 has a higher heat-resistant than PET or PEN polymer substrates, thus would be more feasible to produce photoanodes at a higher temperature. But the processing temperature would still need to be maintained lower than that employed for glass substrate-based devices (usually $\sim 500^\circ\text{C}$). Alternatively, metal substrates such as stainless steel [60–62] and Ti foil [63] have attracted a lot of interests as they are flexible and can sustain high temperature sintering. However, as the metal substrate is not transparent, the device required to be illuminated from the back side, in which case some photons would be lost due to the absorption of counter electrode materials (mainly Pt) and the electrolyte. To resolve this issue, semi-transparent metal meshes have been employed as substrates to allow front illumination [64].

Zou et al. has made an interesting wire based flexible device where a metal wire was coated with TiO_2 and adsorbed dyes as a working electrode, and another wire was coated with Pt as a counter electrode [65]. The metal wire offers high flexibility and good conductivity. The two wires were twisted together and filled with electrolyte to form a device as shown in Figure 9 (a, b). Based on this novel idea, they developed a fiber-shaped weave-able DSSC, in which a thinner counter electrode wire twisted on the working electrode wire, as shown in Figure 9 (c, d) [66] and a bifacial wired flexible DSSC, in which the counter electrode wire and working electrode wire were paralleled alternately, as shown in Figure 9 (e, f) [67].

As the metal wire is non-transparent for the light, alternatively, optical fibers have been employed as the substrate [68]. Firstly, a ZnO:Al film of 130 nm was deposited on the fiber by atomic layer deposition to introduce a conductive coating. Then a mesoporous TiO_2 film was coated and sensitized with dyes. After adding the gelatinized iodine electrolyte by dip-coating, the carbon-based counter electrode was coated to complete the device. By this configuration, the light can travel along the optical fiber and be scattered to the sensitized electrode to generate photocurrent. Weintraub et al. [69] have coated

ZnO nanowires on the optical fiber to prepare a 3D fiber-based DSSC device, as shown in Figure 10. The device gave a higher power output when light illuminated from the core of the optical fiber than from the side. By the 3D design, the light interaction surface area is increased and then the device performance was greatly improved. The efficiency of the fiber based 3D DSSC device was 120% higher than that of ZnO nanowire devices made on the flat substrate.

Various different film processing techniques have been successfully demonstrated by different research groups around the world. Table 1 is a summary for a number of film deposition and processing techniques used for the preparation of DSSCs on plastic substrates and the corresponding power conversion efficiency of the devices.

Low temperature fabrication of counter electrodes on plastic substrates

As one of the main components in DSSCs, counter electrode plays a very important function in the process of photo-to-electricity conversion. Similar to the working electrode, a number of issues arise when counter electrodes are prepared on plastic substrates. As the high temperature process is not allowed, the deposition of counter electrode materials on plastic substrates requires novel low temperature methods different to conventional high temperature methods used in the glass-based counter electrodes. Sputter coating of Pt on flexible substrates is a widely used technique reported in the literature; however this is a relatively expensive approach. In order to reduce the cost, counter electrode materials other than Pt, such as carbon [71–74], graphene [75,76], carbon nanotubes [77], poly(3,4-ethylenedioxythiophene) (PEDOT) [78–80], and CoS [80,81], and other deposition techniques have been employed for making counter electrodes.

Low temperature deposition

In general, counter electrode materials/precursors are prepared in a slurry/solution, and then coated onto plastic substrates by different coating techniques, followed by a low temperature annealing process. H_2PtCl_6 is a commonly

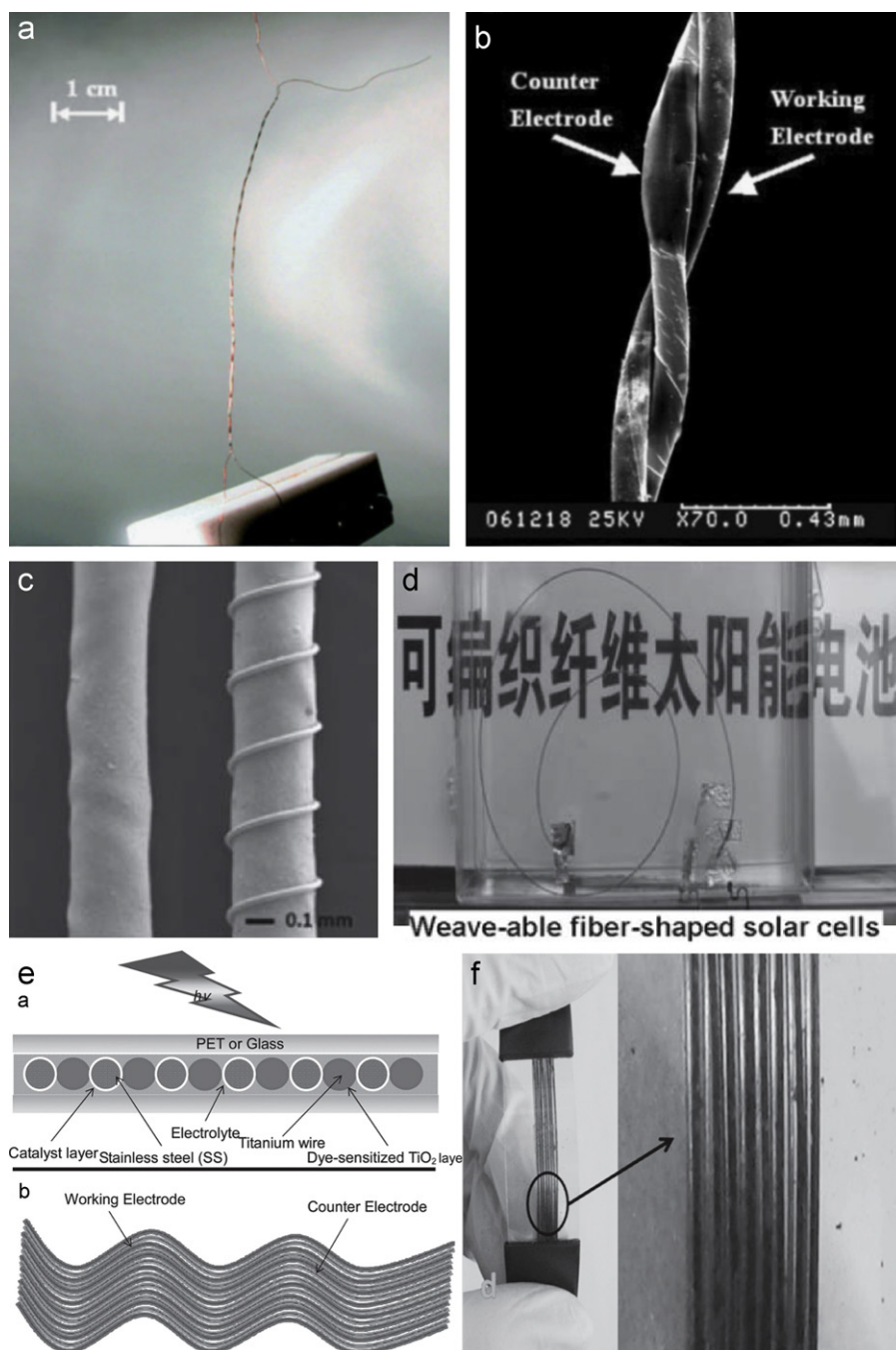


Figure 9 (a) Optical photo of a twisted WSF-DSSC (Uncut; radius= ~ 0.2 mm), (b) SEM photo of a WSF-DSSC [65], (c) SEM of the fiber-shaped solid state photoanode with (right) and without (left) the counter electrode, (d) optical image of the fiber-shaped solar cell with length of 30 cm and remarkable flexibility [66], (e) cross section and sketch of a flexible solar cell [67] and (f) photograph of a solar-cell module with an area of 1.50 cm^2 ($0.50 \text{ cm} \times 3.0 \text{ cm}$) [67].

used precursor used to produce a Pt coating on substrates for counter electrodes in DSSCs. To prepare Pt counter electrode on a conductive plastic substrate, H_2PtCl_6 can be coated on the substrate followed by thermal decomposition or chemical reduction. For example, in a vacuum environment, H_2PtCl_6 can be decomposed to form Pt by heating at 120°C for 2 h [82]. Following this method, a platinum/single-wall carbon nanotube (Pt/SWCNT) film has been sprayed onto the conductive plastic substrate to form an effective counter electrode [82]. Except for the

thermal decomposition, Pt counter electrodes can also be made by chemically reducing H_2PtCl_6 . By dip-coating the substrate in Sn^{2+} and H_2PtCl_6 solutions alternately, a Pt layer has been coated on a conductive plastic substrate [83]. Sun et al. [84] employed ethylene glycol as a solvent and a reduction agent for H_2PtCl_6 and made a Pt counter electrode at 180°C . In another process, H_2PtCl_6 /terpineol solutions were screen printed on conductive plastic substrates and then reduced by treating it in a NaBH_4 solution followed by a hydrothermal treatment at 100°C [85].

Carbon based materials have demonstrated excellent catalytic properties and thus are attractive less-expensive alternatives to Pt for DSSC applications. They can be made into counter electrodes on plastic substrates in low temperature annealing processes. A polypyrrole/*f*-MWCNT (multiwalled carbon nanotubes) aqueous slurry has been drop-casted on an ITO-PEN film, and dried at 60 °C under vacuum to form a counter electrode [86]. The resulted films have exhibited improved adhesion with the plastic substrate. A flexible DSSC device made from such counter electrodes showed a PCE of 4.0% (Figure 11 [86]). Although the efficiency is lower than that of Pt counter electrode, this method showed a facile process to prepare counter electrodes and a further increase in PCE was expected by optimizing the thickness of the counter electrode film. Carbon-nanofiber was also made as a counter electrode by a doctor-blading technique, followed by annealing at 100 °C for 5 h in a vacuum oven [71]. Such counter electrodes showed a quite comparable catalytic property as a Pt counter electrode on glass. However, due to the low temperature annealing process, higher sheet resistance in

the counter electrode was reported, which would compromise the fill factor of the prepared devices [86].

Electrochemical deposition

As a room temperature processing technique, the electrochemical deposition method has attracted a lot of interests [87-90]. Counter electrodes deposited by the electrochemical method can possess high conductivity due to improved adhesion between the counter electrode film and the substrate. Compared to many other deposition techniques, electrochemical deposition is limited to produce relatively thin films. However, this would not be a major obstacle for DSSC applications, in which the counter electrode is normally less than 10 µm thick.

The counter electrodes have also been prepared by means of direct current (DC) and pulse current (PC) electrodeposition methods. Normally, the PC electrodeposition method was preferred as it showed some advantages of controllable particle size, stronger adhesion, reduced internal stress and uniform film morphology compared to the DC electrodeposition. By applying a pulse current in an H_2PtCl_6 solution, uniform Pt nanoclusters of ~40 nm composed of 3 nm particles were coated on plastic substrates [87]. Similarly, a CoS counter electrode on a plastic substrate was produced by placing the substrate in an alkaline (pH=10) aqueous solution containing 5 mM cobalt(II) chloride and 150 mM thiourea, with a potential of -0.8 V vs. Ag/AgCl [81]. The resulted counter electrode was tested for flexible DSSC devices and showed a PCE of 6.5% in conjunction with a Z907 sensitizer and a eutectic melt electrolyte. The performance of the CoS counter electrode is comparable to that of the device made from Pt counter electrode [81].

Electrophoretic deposition described in the previous sections is another electrochemical deposition method successfully utilized for the preparation of counter

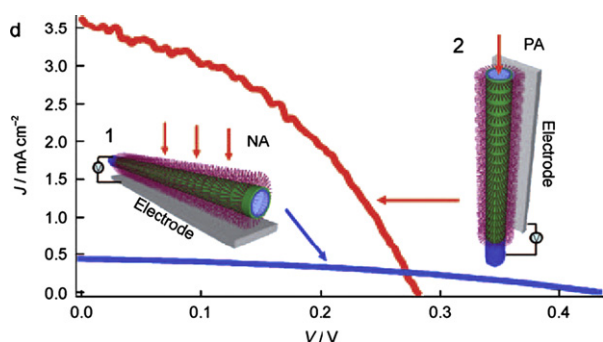


Figure 10 J-V curves of the fiber-based DSSC under one full-sun illumination (AM 1.5 illumination, 100 mW cm⁻²) [69]. The illumination is (1) normal to the fiber axis (NA; 2D case) and (2) parallel to the fiber axis (PA; 3D case).

Table 1 A brief summary of different film deposition and processing techniques used for preparation of DSSCs on plastic substrates.

Paste	Pre-treatment	Deposition technique	Post-treatment	PCE (%)	Ref.
TiO ₂ , water	None	Doctor blading	Mechanical pressing	8.1	[47]
TiO ₂ beads	TiCl ₄ treatment	Doctor blading	CIP compression	7.5	[51]
TiO ₂ P25, ethanol	None	Doctor blading	CIP compression	6.3	[39]
TiO ₂ P25, ethanol, acetylacetone, iodine, acetone, and water additives	None	Electrophoretic deposition	Compression	6.2	[33]
TiO ₂ P25, ethanol	Acid, base treatment	Doctor blading	None	5	[21]
TiO ₂ P25, ethanol, water	None	Doctor blading	None	4.9	[20]
TiO ₂ P25, ethanol	Ball milling	Doctor blading	None	4.2	[11]
TiO ₂ (F-5, G-2 from Showa Denko)	None	Electrophoretic deposition	UV treatment	4.1	[70]
TiO ₂ 100 nm and 12 nm particles, TiO ₂ P25, butanol	None	Doctor blading	Chemical sintering	3.1	[26]
TiO ₂ (TAYCA Corp., TKS-201)	Hydrothermal	Doctor blading	Microwave heating	2.2	[45]
TiO ₂ P25, ethanol, hydroxybenzoic acid	Pre-sintering	Spray-dried	None	2.1	[37]

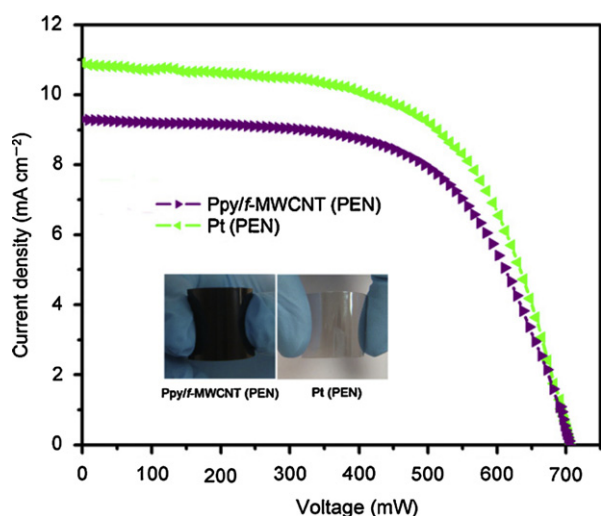


Figure 11 Photocurrent density-voltage curves (J-V) of DSSCs with Ppy/f-MWCNT and Pt films on PEN substrates as the counter electrodes under AM1.5 illumination of 100 mW cm^{-2} , respectively. The inset shows photos of Pt (left) and Ppy/f-MWCNT (right) films on PEN substrates [84].

electrodes on plastic substrates. For example, an efficient counter electrode has been prepared on a plastic ITO-PEN substrate, by immersing in a platinum colloid solution with an applied d.c field of 1.6 V cm^{-1} followed by a heat-treatment at 60°C for 30 min to remove water and ethanol. Flexible DSSCs prepared using the counter electrodes deposited by this method have shown higher PCE (5.8%) compared to the counter electrodes prepared by the sputter-coating method (5.3%) [89].

Similar to the electrophoretic deposition method, counter electrodes on plastics substrates can also be fabricated by a simple electrospinning technology. In a typical synthesis, an electrospinning solution, for example, a mixture of Polyaniline emeraldine (PANI), 10-camphorsulfonic acid (CSA) and polylactic acid (PLA) in chloroform was loaded into a plastic syringe, and then electrospun at a rate of 1.0 mL h^{-1} and an electric field of 25 kV. The conductive plastic substrates were placed onto an aluminum collector to collect films and the thickness of the film is controlled by the electrospinning time [90]. This method can provide a fast and facile fabrication of low-cost counter electrodes on plastic substrates and is suitable for potential roll-to-roll production.

Other deposition methods

A pulsed laser deposition method has been employed to deposit graphite onto conductive plastic substrates as a low-cost alternative to platinum for the counter electrode [91]. The properties of the pulsed laser deposited films can be adjusted by tuning of experimental variables such as laser pulse width, wavelength, ablation time, substrate-target distance, laser fluence, and inert gas pressure [91]. Wan et al. adopted a transferring technique to coat graphene counter electrode on the conductive plastic substrate [92]. Graphene dispersion has been vacuum filtrated using a mixed cellulose ester membrane and the resulted membrane with graphene has been transferred and adhered on

to the plastic substrate under a pressure applied by a heavy weight. Similarly, Lee et al. employed a “growth-detachment-transfer” process to coat vertically aligned N-doped carbon nanotube arrays on the conductive plastic substrate [93].

In order to reduce the cost and to improve the performance of the flexible DSSC, researchers have also tried to replace the expensive ITO coated substrate with other conductive materials at the counter electrode side [94-97]. Wang et al. employed titanium carbide, tungsten oxide, and vanadium nitride as catalysts and at the same time to provide conductivity for electrons [95]. Alternatively, Huang et al. used aligned carbon nanotube/polymer composite films that are transparent, flexible, and highly conductive as the counter electrode [96].

Conductive substrates and blocking layers

Conductive substrates

In flexible DSSCs, a TiO_2 porous film is coated on a conductive substrate, usually ITO coated PET or PEN. ITO is a quite expensive material due to large demands and relatively low availability. Thus other alternative conductive materials have been studied for the replacement of the ITO layer. Such alternative materials should be transparent, highly conductive, bendable, and non-reactive with the electrolyte. These conductive materials must exhibit low absorption and no scattering for the incident light. Furthermore, high conductivity is required to reduce the sheet resistance of the device, which is one of major factors affecting the PCE of the device. In addition, the conductive layer should demonstrate high endurance on bending deformation, which would confine the thickness of the layer.

Ito et al. demonstrated a $\text{TiO}_2\text{-Ag-TiO}_2$ film as a replacement of the ITO layer, where TiO_2 acts as a dielectric material while Ag providing the required high conductivity [98]. Both materials exhibit low absorption in the visible light region of the solar spectrum. The sputtered layers ($20 \text{ nm TiO}_2/10 \text{ nm Ag}/100 \text{ nm TiO}_2$) had sheet resistance of $8 \Omega/\square$, average transmittance of 82% and reflectance (400-700 nm) of 6.3%, and showed higher PCE compared to the DSSC devices fabricated on FTO and ITO substrates [98]. Magnetron sputtered aluminum-doped zinc oxide (AZO) films have also been investigated as the conductive layer on plastic substrates. A PCE of 2.1% was achieved in DSSCs with the AZO substrate. This was an inexpensive alternative approach for producing mechanically and chemically stable conductive films on flexible substrates [99].

Blocking layer

In order to inhibit the recombination between electrons in the conductive substrate and holes in the electrolyte/hole conductor, normally a pinhole free, extremely thin dense layer is deposited on the top of the conductive layer as a blocking layer [100,101]. On the glass substrate, this is normally achieved by spray pyrolysis of titanium di-isopropoxide bis-(acetylacetonate) solution [102] or by immersing the substrates in chemical bath of TiCl_4 aqueous solution [55]. Both these processes require high temperature heat treatment

(>400 °C) for converting amorphous TiO₂ to crystals, and thus are not suitable for plastic substrates. However several techniques have been attempted for the preparation of a blocking layer at low processing temperatures although they are still not fully desirable to be used in flexible DSSCs. Dip-coating method followed by the microwave treatment has been attempted by Hart et al. [103] to prepare a dense TiO₂ layer at low temperatures. A TiO₂ barrier layer has also been prepared by the sputtering and e-beam evaporation methods [104]. Furthermore, Chen et al. [105] have prepared an ultrathin layer of TiO₂ on the conductive plastic substrate by sputtering a TiO₂ target, and found that the addition of the compact layer increased the PCE by more than 25%. More efforts in this area are required to develop an effective blocking layer on plastic substrates in order to adapt newly developed electrolytes, such as cobalt based systems and other solid-state hole-transport materials efficiently used on glass-based DSSCs.

Stability and up-scaling

Sealing and stability

Poor stability is one of the major issues that render commercialization of DSSCs on flexible substrates. This is mainly caused by the leakage and deterioration of the electrolyte due to imperfections in the sealing material and process [106]. Sealing of the electrolyte between the working and counter electrodes has become a more concerned issue in plastic substrate-based DSSCs due to the poor adhesion of sealing materials with the polymer substrate surface. Thus, when using Surlyn or Bynel materials to seal the two plastic substrates in a device, the films tend to delaminate more easily compared to the glass-based DSSCs. The delamination creates defects in the sealed edges allowing the electrolyte to leak. Thus, alternative sealing materials, such as silicone elastomers and epoxy resins are currently being examined. However, finding a suitable sealing material that can be applied at low temperature and has high resistance to the corrosive components in the electrolyte still remained as a challenge.

Except for screening out of new sealing materials, more attentions have been focussed on the modification of electrolytes. Ikegami et al. [106] found that electrolyte compositions had a significant effect on the devices' long-term stability. Lil, which is a commonly used compound in electrolyte solutions, was found to react with the ITO coating on plastic substrates. Devices with electrolyte containing Lil showed degradation after outdoor exposure of one month. TiO₂ film found to peel-off partially due to the dissolution of the ITO on the substrate. However, the devices made from a Lil-free electrolyte have shown improved performance over 220 h at 55 °C and 95% humidity conditions under dark [102]. On the other hand, solvents usually used in electrolyte solutions are highly volatile and can easily leak through the imperfections in the sealing. Therefore, 3-methoxypropionitrile (MPN) as a non-volatile solvent with high boiling point and low vapor pressure has been used as a solvent for electrolytes used in plastic based devices. Flexible devices containing MPN as the solvent have achieved PCE above 5%, and are comparable to the PCE

obtained in the commonly used acetonitrile based devices [18]. Lee et al. [107] have investigated the long-term stability of the flexible DSSC using an MPN based electrolyte and found that the performance of the devices maintained 96.9% after more than 1000 h prolonged aging under one sun light irradiation at 60 °C. Furthermore, solvent-free ionic liquid based electrolytes have also been studied in flexible DSSCs [81,108,109]. Flexible devices made from ionic liquid electrolytes have retained 85% of its initial PCE after 1000 h of light soaking at 60 °C [81].

To prevent potential leakage of solvent based electrolytes, quasi-solid-state or solid-state flexible DSSCs have been developed by introducing polymer gels into the electrolytes or by replacing the liquid electrolyte with a solid-state polymer hole conductor [110-120]. Lee et al. [113] used a poly(ethylene oxide)-based gel electrolyte for solidifying flexible DSSCs and incorporated quaternized ammonium iodide-containing conjugated polymer electrolytes (CPEs), in which the ion-supporting side chains supplied channels for ion transport and the polymer backbones provided pathways for hole transporting back to the contact electrode. After the device was operated for 100 h, the PCE dropped merely by 15%. By using the gel electrolyte, a new approach could be developed to laminate flexible DSSCs, in which a gel electrolyte sheet could be laminated between a TiO₂ electrode and the counter-electrode to form a device [110].

Modules and up-scaling

A single flexible DSSC device can only produce 0.6-0.8 V and ~10 mA/cm². The amount of power generated by such a single device has limited usage in real applications. Therefore, different types of modules are required to produce sufficient power for applications. A module in parallel connection can provide a high current for powering small electronics, and that in series connection can offer a high voltage for charging batteries. By combining the different types of modules to form a large area device, it can provide both high voltage and current. When the device becomes large with high current, it requires a low internal resistance, to minimize the energy lost through the thermal effect associated with high resistance, which in turn would damage the device. Normally, a metal grid that has high endurance to the corrosive electrolyte corrosion is coated between the working electrode strips to collect and transport photogenerated current. Miyasaka [121] have made DSSC modules on plastic substrate, which produced 7.2 V as open-circuit photovoltage and 250-300 mA as short-circuit photocurrent. His group has also fabricated large modules producing a stable DC voltage more than 110 V under indoor illumination [122].

DSSCs on plastic substrates have advantages of light weight and thin body compared with glass substrate-based DSSCs. However, a more significant advantage is the flexibility, which not only opens more possible applications, but also makes the mass production much easier. Attempts have been made in producing flexible modules by printing techniques (Figure 12). The roll-to-roll process, commonly employed in the printing industry, can be used to fabricate the flexible DSSCs in a fast production line. For such a process, all layer components consisting of the devices would be printable. This offers a very attractive prospect for mass production of low cost photovoltaic devices.

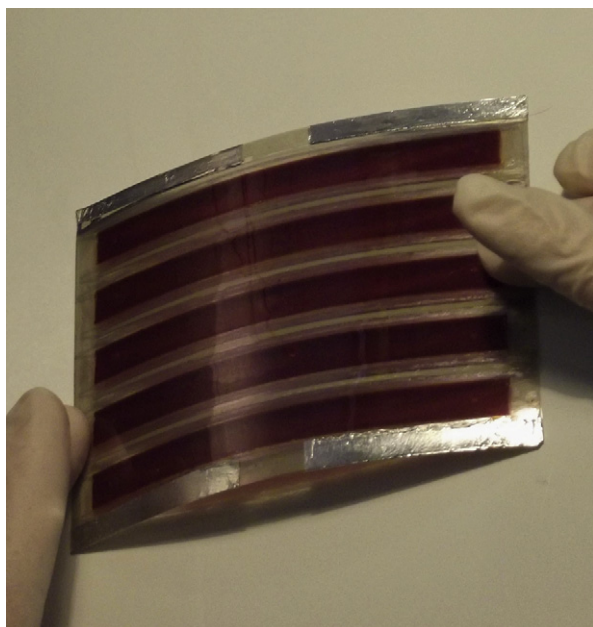


Figure 12 A flexible DSSC module produced by screen printing. (Courtesy to the Victoria Organic Solar Cell Consortium (VICOSC), Australia).

Conclusions and outlook

Plastic substrate-based DSSCs are showing increased potential for commercialization owing to its unique features, such as light weight, flexibility, and the feasibility for roll-to-roll speedy mass production. However, further improvements of power conversion efficiency and stability of DSSCs on plastic substrates would be required before commercial production and applications. The relatively low photovoltaic performance in DSSCs on plastic substrates is mainly attributed to the low temperature processing limited by the thermal stability of the plastic substrate. Various low temperature processing methods have been developed for producing efficient working electrodes and new materials and methods have been studied to develop efficient counter electrodes for plastic DSSCs. With great efforts devoted and more novel methods developed, the PCE of plastic based DSSCs has been continuously improved from 4-5% to 6-7% over the last decade and lately the highest PCE of 8.1% has been reported. Furthermore, many different novel structures have been designed for the flexible photoanodes. The 1D structure semiconductors can be directly grown on the flexible substrate to minimize the difference in processing techniques between glass substrate-based device and flexible substrate-based device, providing a very attractive approach to achieve high performance flexible devices. Promising results published by many research groups have shown that the low temperature prepared counter electrodes have competitive performance as the high temperature treated ones. It is highly expected that in the near future the PCE of plastic based DSSCs would be further improved to a higher level, comparative to the glass-based DSSCs. Despite the fact that the poor stability being a major obstacle for the plastic based DSSCs, robust sealing and encapsulation techniques are being investigated by many research groups to

improve the stability and lifetime of flexible DSSCs by preventing electrolyte evaporation and moisture ingress on to the devices. Another alternative approach to improve the lifetime is to substitute the volatile liquid electrolyte with ionic liquid electrolytes or solid-state hole conductors. Although there has been a little work reported so far on the fully solid-state plastic DSSC due to the difficulty in fabricating the blocking layer, different quasi solid-state hole conductor materials and polymer gel electrolytes have shown promising results in the plastic substrate based DSSCs with much improved stability and considerably high efficiencies. When the fully solid-state hole conductors were applied in the flexible device, it is expected that the stability would be improved further. Some novel designs of the flexible DSSCs like fiber-shape and 3D structures would improve the performance of the devices and broaden the real applications of the flexible devices. Flexible DSSCs printed on plastic substrates are envisaged to be a promising, low cost technology for renewable energy in the future.

References

- [1] P. Wang, S.M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker, M. Grätzel, *Journal of Physical Chemistry B* 107 (2003) 14336-14341.
- [2] S. Noda, K. Nagano, E. Inoue, T. Egi, T. Nakashima, N. Imawaka, M. Kanayama, S. Iwata, K. Toshima, K. Nakada, K. Yoshino, *Synthetic Metals* 159 (2009) 2355-2357.
- [3] X. Xi, Q. Meng, F. Li, Y. Ding, J. Ji, Z. Shi, G. Li, *Solar Energy Materials and Solar Cells* 94 (2010) 623-628.
- [4] M. Tuomikoski, P. Kopola, H. Jin, M. Ylikunnari, J. Hiitola-Keinanen, M. Valimäki, M. Aikio, J. Hast, Roll-to-Roll Manufacturing of Organic Photovoltaic Modules, in: *European Microelectronics and Packaging Conference, IEEE* (2009) 217-220.
- [5] B. Muhsin, J. Renz, K.H. Drue, G. Gobsch, H. Hoppe, *Synthetic Metals* 159 (2009) 2358-2361.
- [6] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeeruddin, E.W.-G. Diau, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, *Science* 334 (2011) 629-634.
- [7] I. Chung, B. Lee, J. He, R.P.H. Chang, M.G. Kanatzidis, *Nature* 485 (2012) 486-489.
- [8] A. Zaban, A. Meier, A.J. Nozik, B.A. Gregg, *Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage IV* 97-13 (1997) 306-316.
- [9] K.D. Benkstein, N. Kopidakis, J. van de Lagemaat, A.J. Frank, *The Journal of Physical Chemistry B* 107 (2003) 7759-7767.
- [10] E.S. Carreras, F. Chabert, D.E. Dunstan, G.V. Franks, *Journal of Colloid and Interface Science* 313 (2007) 160-168.
- [11] H.C. Weerasinghe, P.M. Sirimanne, G.P. Simon, Y.B. Cheng, *Journal of Photochemistry and Photobiology a-Chemistry* 206 (2009) 64-70.
- [12] C.Y. Jiang, X.W. Sun, K.W. Tan, G.Q. Lo, A.K.K. Kyaw, D.L. Kwong, *Applied Physics Letters* 92 (2008) 143101.
- [13] Y. Li, K. Yoo, D.-K. Lee, J.H. Kim, N.-G. Park, K. Kim, M.J. Ko, *Current Applied Physics* 10 (2010) E171-E175.
- [14] A.D. Pasquier, M. Stewart, T. Spittler, M. Coleman, *Solar Energy Materials and Solar Cells* 93 (2009) 528-535.
- [15] H.-W. Chen, C.-Y. Hsu, J.-G. Chen, K.-M. Lee, C.-C. Wang, K.-C. Huang, K.-C. Ho, *Journal of Power Sources* 195 (2010) 6225-6231.
- [16] T. Miyasaka, N. Ikeda, T.N. Murakami, K. Teshima, *Chemistry Letters* 36 (2007) 480-487.
- [17] D. Zhang, J.A. Downing, F.J. Knorr, J.L. McHale, *The Journal of Physical Chemistry B* 110 (2006) 21890-21898.
- [18] Y. Kijitori, M. Ikegami, T. Miyasaka, *Chemistry Letters* 36 (2007) 190-191.

- [19] N.G. Park, K.M. Kim, M.G. Kang, K.S. Ryu, S.H. Chang, Y.J. Shin, *Advanced Materials* 17 (2005) 2349-2353.
- [20] H.C. Weerasinghe, G.V. Franks, J.D. Plessis, G.P. Simon, Y.-B. Cheng, *Journal of Materials Chemistry* 20 (2010) 9954-9961.
- [21] H.C. Weerasinghe, P.M. Sirimanne, G.V. Franks, G.P. Simon, Y.B. Cheng, *Journal of Photochemistry and Photobiology A: Chemistry* 213 (2010) 30-36.
- [22] N.-G. Park, M.G. Kang, K.S. Ryu, S.H. Chang, Y.-J. Shin, *Advanced Materials* 17 (2005) 2349-2353.
- [23] D. Zhang, T. Yoshida, H. Minoura, *Chemistry Letters* (2002) 874-875.
- [24] D. Zhang, T. Yoshida, K. Furuta, H. Minoura, *Journal of Photochemistry and Photobiology A: Chemistry* 164 (2004) 159-166.
- [25] T. Miyasaka, M. Ikegami, Y. Kijitori, *Journal of The Electrochemical Society* 154 (2007) A455-A461.
- [26] X. Li, H. Lin, J.B. Li, N. Wang, C.F. Lin, L.Z. Zhang, *Journal of Photochemistry and Photobiology A: Chemistry* 195 (2008) 247-253.
- [27] H.-W. Chen, K.-C. Huang, C.-Y. Hsu, C.-Y. Lin, J.-G. Chen, C.-P. Lee, L.-Y. Lin, R. Vittal, K.-C. Ho, *Electrochimica Acta* 56 (2011) 7991-7998.
- [28] H.-W. Chen, C.-P. Liang, H.-S. Huang, J.-G. Chen, R. Vittal, C.-Y. Lin, K.C.W. Wu, K.-C. Ho, *Chemical Communications* 47 (2011) 8346-8348.
- [29] W.-H. Chiu, K.-M. Lee, W.-F. Hsieh, *Journal of Power Sources* 196 (2011) 3683-3687.
- [30] T. Miyasaka, Y. Kijitori, T.N. Murakami, N. Kawashima, *Proceedings of the Society of Photo-Optical Instrumentation Engineers* 5215 (2004) 219-225.
- [31] T. Miyasaka, Y. Kijitori, T.N. Murakami, M. Kimura, S. Uegusa, *Chemistry Letters* (2002) 1250-1251.
- [32] J.H. Yum, S.S. Kim, D.Y. Kim, Y.E. Sung, *Journal of Photochemistry and Photobiology A: Chemistry* 173 (2005) 1-6.
- [33] L. Grinis, S. Kotlyar, S. Ruhle, J. Grinblat, A. Zaban, *Advanced Functional Materials* 20 (2010) 282-288.
- [34] T. Miyasaka, T.N. Murakami, *Applied Physics Letters* 85 (2004) 3932-3934.
- [35] T.N. Murakami, Y. Kijitori, N. Kawashima, T. Miyasaka, *Chemistry Letters* 32 (2003) 1076-1077.
- [36] J. Halme, J. Saarinen, P. Lund, *Solar Energy Materials and Solar Cells* 90 (2006) 887-899.
- [37] S.I. Cha, B.K. Koo, K.H. Hwang, S.H. Seo, D.Y. Lee, *Journal of Materials Chemistry* 21 (2011) 6300-6304.
- [38] H. Pan, S.H. Ko, N. Misra, C.P. Grigoropoulos, *Applied Physics Letters* 94 (2009) 071117.
- [39] H.C. Weerasinghe, P.M. Sirimanne, G.P. Simon, Y.-B. Cheng, *Progress in Photovoltaics: Research and Applications* 20 (2012) 321-332.
- [40] D. Gutiérrez-Tauste, I. Zumeta, E. Vigil, M.A. Hernández-Fenollosa, X. Domènech, J.A. Ayllón, *Journal of Photochemistry and Photobiology A: Chemistry* 175 (2005) 165-171.
- [41] T.N. Murakami, Y. Kijitori, N. Kawashima, T. Miyasaka, *Journal of Photochemistry and Photobiology A: Chemistry* 164 (2004) 187-191.
- [42] T. Oekermann, D. Zhang, T. Yoshida, H. Minoura, *Journal of Physical Chemistry B* 108 (2004) 2227-2235.
- [43] T. Clark, J.D. Ruiz, H. Fan, C.J. Brinker, B.I. Swanson, A.N. Parikh, *Chemistry of Materials* 12 (2000) 3879-3884.
- [44] G. Mincuzzi, L. Vesce, A. Reale, A.D. Carlo, T.M. Brown, *Applied Physics Letters* 95 (2009) 103312.
- [45] S. Uchida, M. Timiha, H. Takizawa, M. Kwaraya, *Journal of Photochemistry and Photobiology A: Chemistry* 164 (2004) 93-96.
- [46] H. Lindström, A. Holmberg, E. Magnusson, L. Malmqvist, A. Hagfeldt, *Journal of Photochemistry and Photobiology A: Chemistry* 145 (2001) 107-112.
- [47] T. Yamaguchi, N. Tobe, D. Matsumoto, T. Nagai, H. Arakawa, *Solar Energy Materials and Solar Cells* 94 (2010) 812-816.
- [48] H. Santa-Nokki, J. Kallioinen, T. Kololuoma, V. Tuboltsev, J. Korppi-Tommola, *Journal of Photochemistry and Photobiology A: Chemistry* 182 (2006) 187-191.
- [49] Y. Peng, J.Z. Liu, K. Wang, Y.-B. Cheng, *International Journal of Photoenergy* 2011 (2011) 410352.
- [50] M. Dürr, A. Schmid, M. Obermaier, S. Rosselli, A. Yasuda, G. Nelles, *Nature Materials* 4 (2005) 607-611.
- [51] F. Huang, D. Chen, Q. Li, R.A. Caruso, Y.-B. Cheng, *Applied Physics Letters* 100 (2012) 123102.
- [52] F.Z. Huang, D.H. Chen, X.L. Zhang, R.A. Caruso, Y.B. Cheng, *Advanced Functional Materials* 20 (2010) 1301-1305.
- [53] D.H. Chen, L. Cao, F.Z. Huang, P. Imperia, Y.B. Cheng, R.A. Caruso, *Journal of the American Chemical Society* 132 (2010) 4438-4444.
- [54] D.H. Chen, F.Z. Huang, Y.B. Cheng, R.A. Caruso, *Advanced Materials* 21 (2009) 2206-2210.
- [55] F. Sauvage, D.H. Chen, P. Comte, F.Z. Huang, L.-P. Heiniger, Y.B. Cheng, R.A. Caruso, M. Grätzel, *ACS Nano* 4 (2010) 4420-4425.
- [56] C.R. Ke, J.M. Ting, *Journal of Power Sources* 208 (2012) 316-321.
- [57] B.C. O'Regan, J.R. Durrant, P.M. Sommeling, N.J. Bakker, *Journal of Physical Chemistry C* 111 (2007) 14001-14010.
- [58] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P.D. Yang, *Nature Materials* 4 (2005) 455-459.
- [59] A. Vomiero, V. Galstyan, A. Braga, I. Concina, M. Brisotto, E. Bontempi, G. Sberveglieri, *Energy & Environmental Science* 4 (2011) 3408-3413.
- [60] Y. Jun, J. Kim, M.G. Kang, *Solar Energy Materials and Solar Cells* 91 (2007) 779-784.
- [61] J.H. Park, Y. Jun, H.-G. Yun, S.-Y. Lee, M.G. Kang, *Journal of the Electrochemical Society* 155 (2008) F145-F149.
- [62] X. Huang, P. Shen, B. Zhao, X. Feng, S. Jiang, H. Chen, H. Li, S. Tan, *Solar Energy Materials and Solar Cells* 94 (2010) 1005-1010.
- [63] M.G. Kang, N.G. Park, K.S. Ryu, S.H. Chang, K.J. Kim, *Chemistry Letters* 34 (2005) 804-805.
- [64] X. Fan, F. Wang, Z. Chu, L. Chen, C. Zhang, D. Zou, *Applied Physics Letters* 90 (2007) 073501.
- [65] X. Fan, Z. Chu, F. Wang, C. Zhang, L. Chen, Y. Tang, D. Zou, *Advanced Materials* 20 (2008) 592-595.
- [66] D. Wang, S. Hou, H. Wu, C. Zhang, Z. Chu, D. Zou, *Journal of Materials Chemistry* 21 (2011) 6383-6388.
- [67] Y. Fu, Z. Lv, S. Hou, H. Wu, D. Wang, C. Zhang, D. Zou, *Advanced Energy Materials* 2 (2012) 37-41.
- [68] M. Toivola, M. Ferenets, P. Lund, A. Harlin, *Thin Solid Films* 517 (2009) 2799-2802.
- [69] B. Weintraub, Y.G. Wei, Z.L. Wang, *Angewandte Chemie-International Edition* 48 (2009) 8981-8985.
- [70] T. Miyasaka, Y. Kijitori, *Journal of the Electrochemical Society* 151 (2004) A1767-A1773.
- [71] G. Veerappan, W. Kwon, S.-W. Rhee, *Journal of Power Sources* 196 (2011) 10798-10805.
- [72] J. Chen, K. Li, Y. Luo, X. Guo, D. Li, M. Deng, S. Huang, Q. Meng, *Carbon* 47 (2009) 2704-2708.
- [73] B. Zhao, H. Huang, P. Jiang, H. Zhao, X. Huang, P. Shen, D. Wu, R. Fu, S. Tan, *Journal of Physical Chemistry C* 115 (2011) 22615-22621.
- [74] J. Chen, B. Li, J. Zheng, J. Zhao, H. Jing, Z. Zhu, *Electrochimica Acta* 56 (2011) 4624-4630.
- [75] K.S. Lee, Y. Lee, J.Y. Lee, J.-H. Ahn, J.H. Park, *ChemSusChem* 5 (2012) 379-382.
- [76] J.D. Roy-Mayhew, D.J. Bozym, C. Punckt, I.A. Aksay, *ACS Nano* 4 (2010) 6203-6211.
- [77] R.A. Sayer, S.L. Hodson, T.S. Fisher, *Journal of Solar Energy Engineering-Transactions of the Asme* 132 (2010) 021007.
- [78] A. Kancirzewska, E. Dobruchowska, A. Baranzahi, E. Carlegm, A. Fahlman, M. Fahlman, M.A. Girtu, *Proceedings of the Society of Photo-Optical Instrumentation Engineers* 6656 (2007) 665611.

- [79] A. Kanciurzevska, E. Dobruchowska, A. Baranzahi, E. Carlegrim, M. Fahlman, M.A. Girtu, *Journal of Optoelectronics and Advanced Materials* 9 (2007) 1052-1059.
- [80] P. Sudhagar, S. Nagarajan, Y.-G. Lee, D. Song, T. Son, W. Cho, M. Heo, K. Lee, J. Won, Y.S. Kang, *Acs Applied Materials & Interfaces* 3 (2011) 1838-1843.
- [81] M. Wang, A.M. Anghel, B. Marsan, N.-L.C. Ha, N. Pootrakulchote, S.M. Zakeeruddin, M. Graetzel, *Journal of the American Chemical Society* 131 (2009) 15976-15977.
- [82] Y. Xiao, J. Wu, G. Yue, J. Lin, M. Huang, Z. Lan, *Electrochimica Acta* 56 (2011) 8545-8550.
- [83] X.-L. He, M. Liu, G.-J. Yang, S.-Q. Fan, C.-J. Li, *Applied Surface Science* 258 (2011) 1377-1384.
- [84] K. Sun, B. Fan, J. Ouyang, *Journal of Physical Chemistry C* 114 (2010) 4237-4244.
- [85] L. Chen, W. Tan, J. Zhang, X. Zhou, X. Zhang, Y. Lin, *Electrochimica Acta* 55 (2010) 3721-3726.
- [86] S. Peng, Y. Wu, P. Zhu, V. Thavasi, S.G. Mhaisalkar, S. Ramakrishna, *Journal of Photochemistry and Photobiology a-Chemistry* 223 (2011) 97-102.
- [87] S.S. Kim, Y.C. Nah, Y.Y. Noh, J. Jo, D.Y. Kim, *Electrochimica Acta* 51 (2006) 3814-3819.
- [88] G. Zhu, L. Pan, T. Lu, X. Liu, T. Lv, T. Xu, Z. Sun, *Electrochimica Acta* 56 (2011) 10288-10291.
- [89] X. Yin, Z. Xue, B. Liu, *Journal of Power Sources* 196 (2011) 2422-2426.
- [90] S. Peng, P. Zhu, Y. Wu, S.G. Mhaisalkar, S. Ramakrishna, *Rsc Advances* 2 (2012) 652-657.
- [91] K.P. Acharya, H. Khatri, S. Marsillac, B. Ullrich, P. Anzenbacher, M. Zamkov, *Applied Physics Letters* 97 (2010) 201108.
- [92] L. Wan, S. Wang, X. Wang, B. Dong, Z. Xu, X. Zhang, B. Yang, S. Peng, J. Wang, C. Xu, *Solid State Sciences* 13 (2011) 468-475.
- [93] K.S. Lee, W.J. Lee, N.-G. Park, S.O. Kim, J.H. Park, *Chemical Communications* 47 (2011) 4264-4266.
- [94] S. Hou, X. Cai, Y. Fu, Z. Lv, D. Wang, H. Wu, C. Zhang, Z. Chu, D. Zou, *Journal of Materials Chemistry* 21 (2011) 13776-13779.
- [95] Y. Wang, M. Wu, X. Lin, Z. Shi, A. Hagfeldt, T. Ma, *Journal of Materials Chemistry* 22 (2012) 4009-4014.
- [96] S. Huang, L. Li, Z. Yang, L. Zhang, H. Saiyin, T. Chen, H. Peng, *Advanced Materials* 23 (2011) 4707-4710.
- [97] H. Sun, Y. Luo, Y. Zhang, D. Li, Z. Yu, K. Li, Q. Meng, *Journal of Physical Chemistry C* 114 (2010) 11673-11679.
- [98] S. Ito, T. Takeuchi, T. Katayama, M. Sugiyama, M. Matsuda, T. Kitamura, Y. Wada, S. Yanagida, *Chemistry of Materials* 15 (2003) 2824-2828.
- [99] D.-J. Kwak, J.-H. Kim, B.-W. Park, Y.-M. Sung, M.-W. Park, Y.-B. Choo, *Current Applied Physics* 10 (2010) S282-S285.
- [100] A. Burke, S. Ito, H. Snaith, U. Bach, J. Kwiattkowski, M. Grätzel, *Nano Letters* 8 (2008) 977-981.
- [101] P.J. Cameron, L.M. Peter, *Journal of Physical Chemistry B* 107 (2003) 14394-14400.
- [102] L. Kavan, M. Grätzel, *Electrochimica Acta* 40 (1995) 643-652.
- [103] J.N. Hart, D. Menzies, Y.-B. Cheng, G.P. Simon, L. Spiccia, *Journal of Sol-Gel Science and Technology* 40 (2006) 45-54.
- [104] T.B. Meyer, A.F. Meyer, D. Ginestoux, *Proceedings of the Society of Photo-Optical Instrumentation Engineers* 4465 (2002) 13-20.
- [105] P. Chen, Y.-W. Lo, T.-L. Chou, J.-M. Ting, *Journal of the Electrochemical Society* 158 (2011) H1252-H1257.
- [106] M. Ikegami, J. Suzuki, K. Teshima, M. Kawaraya, T. Miyasaka, *Solar Energy Materials and Solar Cells* 93 (2009) 836-839.
- [107] K.-M. Lee, W.-H. Chiu, M.-D. Lu, W.-F. Hsieh, *Journal of Power Sources* 196 (2011) 8897-8903.
- [108] D. Kuang, J. Brillet, P. Chen, M. Takata, S. Uchida, H. Miura, K. Sumioka, S.M. Zakeeruddin, M. Graetzel, *ACS Nano* 2 (2008) 1113-1116.
- [109] J. Chen, H. Lin, X. Li, X. Zhao, F. Hao, S. Dong, *Electrochimica Acta* 56 (2011) 6026-6032.
- [110] A. Du Pasquier, *Electrochimica Acta* 52 (2007) 7469-7474.
- [111] N. Ikeda, T. Miyasaka, *Chemistry Letters* 36 (2007) 466-467.
- [112] Q. Li, J. Wu, Z. Tang, Y. Xiao, M. Huang, J. Lin, *Electrochimica Acta* 55 (2010) 2777-2781.
- [113] R.-H. Lee, T.-F. Cheng, J.-W. Chang, J.-H. Ho, *Colloid and Polymer Science* 289 (2011) 817-829.
- [114] L.-C. Chen, J.-M. Ting, Y.-L. Lee, M.-H. Hon, *Journal of Materials Chemistry* 22 (2012) 5596-5601.
- [115] M.A. De Paoli, A.F. Nogueira, D.A. Machado, C. Longo, *Electrochimica Acta* 46 (2001) 4243-4249.
- [116] C. Longo, A.F. Nogueira, M.A. De Paoli, H. Cachet, *Journal of Physical Chemistry B* 106 (2002) 5925-5930.
- [117] S.A. Haque, E. Palomares, H.M. Upadhyaya, L. Otley, R.J. Potter, A.B. Holmes, J.R. Durrant, *Chemical Communications* (2003) 3008-3009.
- [118] C. Longo, J. Freitas, M.A. De Paoli, *Journal of Photochemistry and Photobiology A: Chemistry* 159 (2003) 33-39.
- [119] D. Wei, H.E. Unalan, D. Han, Q. Zhang, L. Niu, G. Amaratunga, T. Ryhanen, *Nanotechnology* 19 (2008) 424006.
- [120] K.C. Mandal, A. Smimov, D. Peramunage, R.D. Rauh, *Materials Research Society Symposium Proceedings* 737 (2003) 739-744.
- [121] T. Miyasaka, *Key Engineering Materials* 451 (2011) 1-19.
- [122] T. Miyasaka, M. Ikegami, *Journal of Photopolymer Science and Technology* 23 (2010) 269-277.



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