

Wire-Shaped Flexible Dye-Sensitized Solar Cells**

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In the past 20 years, dye-sensitized solar cells (DSSCs) have received more and more attentions from both academia and industry because of their advantages, such as high efficiency, low cost, environment-friendliness, low incident-light-angle dependence, flexibility, and so on. Through continuous development,^[1–5] it was reported that the efficiency ($\eta_{AM1.5}$) of DSSC using fluorine-doped tin oxide (FTO) glass as the substrate of working electrode has exceeded 11 % (100 mW cm^{-2}).^[6,7] However, the rigid FTO glass has restricted DSSCs' adaptability during transportation, installation, and application. In order to strengthen DSSCs' adaptability, the flexible cell has become a challenge. At present, researches on flexible DSSC were carried out mainly on polymer/ITO-composed conducting substrate.^[8–10] The $\eta_{AM1.5}$ of the all-plastic, flat-shaped DSSC with PET/ITO as the working electrode's substrate exceeded 2.3 % (100 mW cm^{-2}).^[11] However, transparent conducting oxide (TCO) materials with both high transparency and high conductivity are difficult to obtain. Along with polymer substrate materials, there come many disadvantages, such as poor heat resistance and fatigue. Gang et al.^[12] reported a flexible DSSC assembled with a flexible stainless steel sheet as the substrate, in which its $\eta_{AM1.5}$ reached 4.2 % (100 mW cm^{-2}). However, they had to use Pt-coated PET/ITO as the counter electrode due to the opacity of the working electrodes. Our team once produced flexible DSSC working electrodes using heat-resistant conducting mesh to replace traditional TCO glasses,^[13] and assemble a flexible liquid DSSC without any TCO in both electrodes. This mesh-like working electrode is cheap, transparent, highly flexible, highly conductive, and possesses a temperature over 500 °C. In the rapid-developing electronic industry, especially in the fields of portable and high-integrated micro-electronic equipment, space provided for a cell is limited and unfavorable in terms of its shape, or even could be changing constantly. To further develop a photovoltaic device, which can

meet these requirements, weaveable wire-shaped flexible dye-sensitized solar cells (WSF-DSSCs) can be a good solution.

In this Communication, we report a type of WSF-DSSC. The cell has a simple helical twisting structure formed by two fiber-like electrodes. Thanks to the twisting structure, many opaque conducting materials such as metal wires can be successfully applied. This flexible and very fine photovoltaic device also processes some interesting properties for photo sensors.

Figure 1a shows an optical photo of a 5 cm long WSF-DSSC. Figure 1b–d are the SEM photos of WSF-DSSC without the electrolyte. The working electrode is stainless steel fiber coated with a layer of dye-sensitized porous TiO_2 . The counter electrode could be conducting fiber, such as Pt wire, coated with a polymer protective layer (PPL). Because of the twisting structure of the two electrodes, the light can easily reach the working electrode. The cell's apparent diameter was about 200 μm . The entire cell was still a very fine wire with good flexibility. By changing the fibrous substrate, finer and more flexible cells could be further developed. Since the working electrode and counter electrode are twisted together symmetrically, it is predicted that the cell's illumination state remains the same regardless of whether the incident light comes from any direction normalized to the twisting axis. Figure 2a shows the I_{sc} (short-circuit current) of a WSF-DSSC at different rotating degrees around or parallel to the twisting central axis, when the incident light's intensity remains the same. The figure shows that the I_{sc} rarely changed when the incident angles changed. The angle dependence of WSF-DSSC's IV output on incident light is extremely low, which brings convenience for the installation of a photovoltaic device module. It could also make a convenient photo-sensor for light intensity measurement.

The electrode's twisting process greatly influences the performance of WSF-DSSC. During the twisting process, high local pressure is easily produced between electrodes due to local stress concentration on certain parts. In these local parts, the carriers' back-transfer rate increases, which results in the reduction of voltage and current. At different twisting states, the stress state between electrodes will also change accordingly. To relieve local stress, we have tried to coat PPL on the surface of the counter electrode. In Figure 2b, the IV curves of cells with different twisting states are summarized. Here, \times represents a cell without PPL and the twisting screw-pitch is 3 mm. Others represent cells with a 30 μm -thick PVDF, but the twisting screw-pitches are different. The figure indicates the importance of PPL. With PPL, both open circuit voltage

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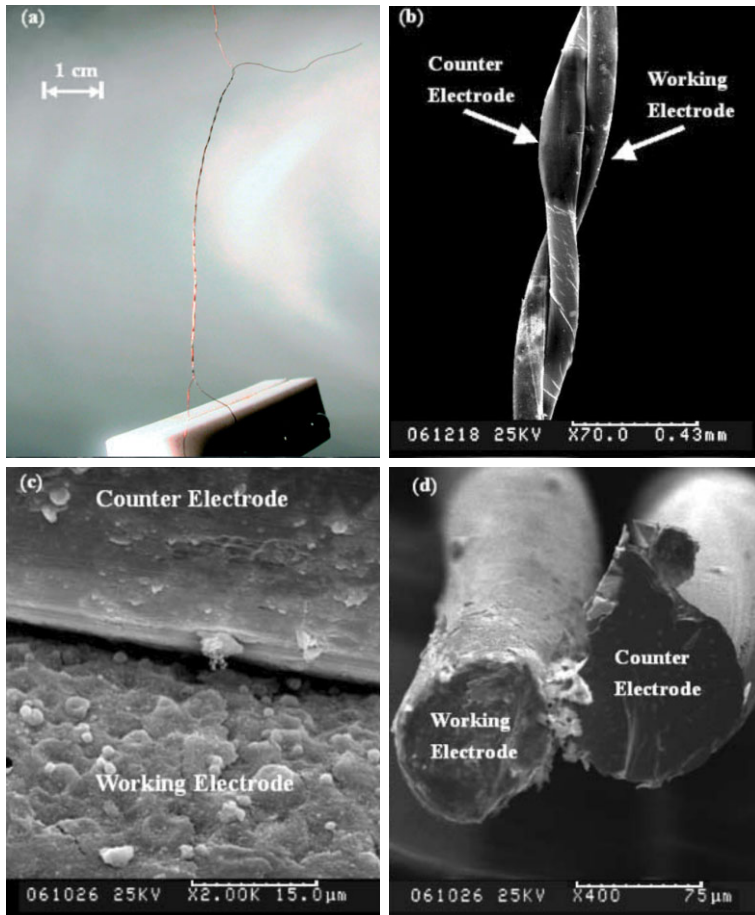


Figure 1. a) Optical photo of a twisted WSF-DSSC (Uncut; Radius: ~ 0.2 mm); b) and c) SEM photo of a WSF-DSSC (top view); d) SEM photo of a WSF-DSSC (sectional view);

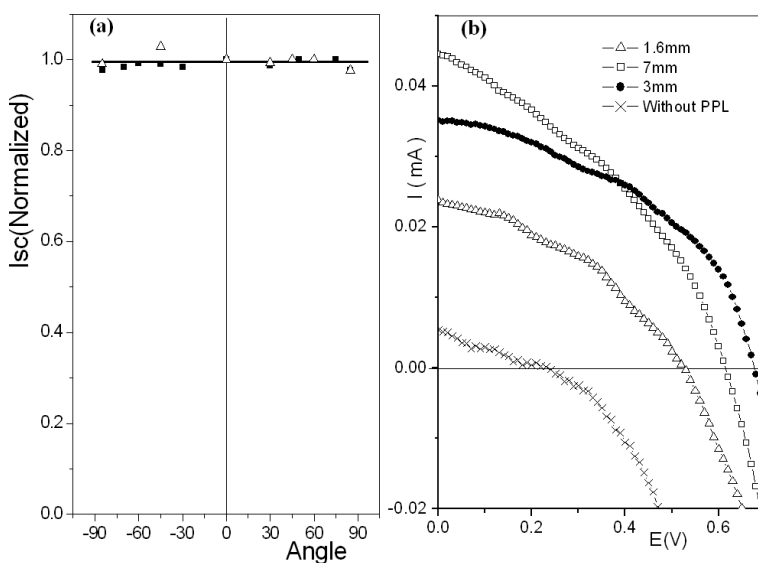


Figure 2. a) I_{sc} (normalized) vs. incident angles of light; Rotating \blacksquare around, and \triangle parallel to the twisting axes. b) IV curves of cells with different twisting screw-pitch \triangle 1.6mm; \bullet 3mm; \square 7mm; \times Without PPL.

and short circuit current apparently increase. The soft polymer materials could relieve the stress concentration between the two electrodes through elastic deformation within a certain range of pressure, which suppressed the back-transfer of the carrier. The figure also indicates that with a shortened twisting screw-pitch, the cell's open-circuit voltage (V_{oc}) decrease slowly, and the I_{sc} increase at first and decrease later on. The reason is that when they are twisted loosely, the distance between the two electrodes is longer; the transfer distance of the carriers inside the cell is farther which results in higher inner resistance. If the twisting is too tight, although the PPL could release some local stress, the carrier's back-transfer rate to some extent increased. It is believed that the cell performance will be further improved after optimization of PPL's materials and structure.

We have also found that the conducting fiber's surface porous TiO_2 layer (PTL) structure will not only affect the dye's adsorption but also exert a great influence on the kinetic behaviors of carriers inside the cell. Since the fiber's specific surface is greater than that of the flat-type, this influence will also be greater. Figure 3a shows the IV features of the cell with different thickness of PTL. When the PTL is quite thin, the cell's V_{oc} does not change much when the thickness of PTL increased. Thanks to the increase of the dye's adsorption, the I_{sc} would increase gradually. When the PTL is $3.5 \mu m$ thick, the V_{oc} , I_{sc} and fill factor of the WSF-DSSC are 610 mV, 0.06 mA, and 0.38, respectively. However, when the thickness of the PTL continues increasing, V_{oc} will drop considerably, and I_{sc} 's increasing speed will slow down and finally the I_{sc} begins to drop. In order to study its kinetic behaviors, we compared the light response curves of cells' V_{oc} with different PTL thickness. The experimental results are shown in Figure 3b. In this figure, the solid line indicates the light intensity that changes with time and all other curves are normalized while taking their final V_{oc} as the base. From Figure 3b, it is observed that when the PTL is thin, a peak appears on the curve, and the curve reaches equilibrium finally. When the PTL's thickness increases, the peak disappears gradually, and the curve will finally increase normally. Hence, we believe that the current carriers' kinetic behaviors have been remarkably changed with the increase of the PTL thickness. When a cell is in an open circuit state, the energy level on the electrode interface is decided by both the production rate and back-transfer rate of the photo-generated carriers. The carriers' back-transfer rate is influenced by the electrode's specific surface and oxidation species concentration near the interface, while the back-

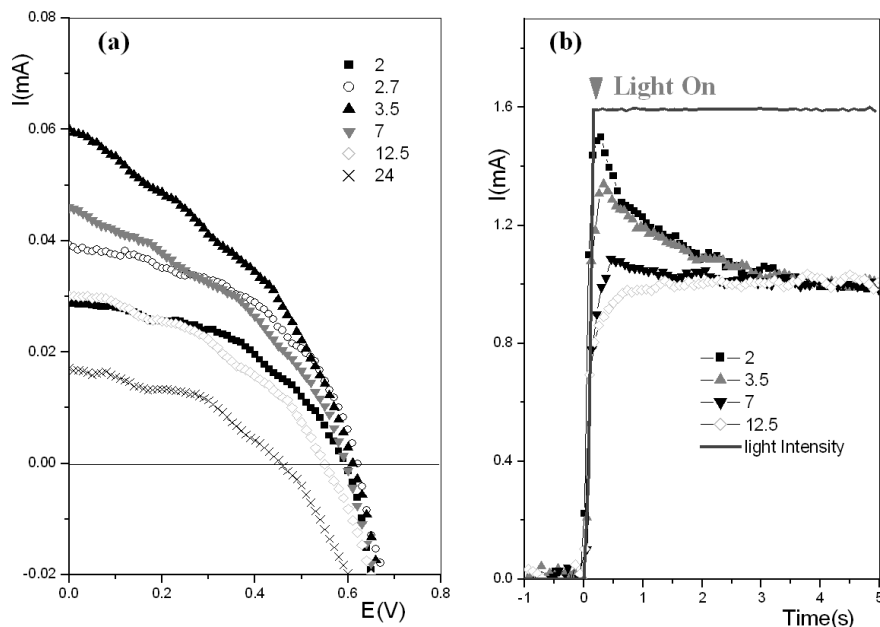


Figure 3. a) IV Curves of DSSCs with different thickness of PTL; b) Response curves of DSSCs with different thickness of PTL; – light intensity; ■ 2 μm ; ○ 2.7 μm ; ▲ 3.5 μm ; ▼ 7 μm ; ◇ 12.5 μm ; × 24 μm .

transfer rate constant is much smaller than the production rate constant.^[14] When the PTL is thin, the electrode's specific surface is small, and the initial back-transfer rate of the current carrier is small as well. At the moment of illumination, a large amount of photo-generated electrons accumulate rapidly within the conduction band of TiO_2 , and the V_{oc} increases rapidly. Afterward, carriers' back-transfer rate begins to increase, for oxidation species are concentrated near the electrode's interface later on, V_{oc} drops gradually and finally reaches an equilibrium state, and a peak appears on the curve. When the thickness of PTL increases, the electrode's specific surface increases, and the initial back-transfer rate of the current carriers gets larger. Thus, it is hard for photo-generated electrons to rapidly accumulate in the conducting band of TiO_2 , and the peak disappears. It only gradually achieves equilibrium due to the charging process of the electrode's interface capacitor. Similarly, V_{oc} and I_{sc} after equilibrium will drop considerably due to the increase of the carriers' back-transfer rate. We believe that cell's performance could be further improved by the optimization of the PTL structure and electrolyte components to make them possess of high dye's adsorption and low carrier back-transfer rate.

Two different WSF-DSSC were combined to work in series or in parallel. Figure 4a are working curves of two cells that worked independently, in series, or in parallel. When two cells worked in series, the total voltage basically equaled the sum of the two cells' respective voltages. When two cells

worked in parallel, the total current outputs basically equaled the sum of the two cells' respective working currents. Figure 4b compares IV features of cells with different lengths. The results indicated that, at least within the length range of our experiments, the cell's I_{sc} increased linearly as the cell grew longer. The conductivity of the metal materials is much higher than TCO, which could ensure the effective transmission of the photo-generated electrons to the outer circuit. This is very important especially for large-area cells. The above results indicate that, via simple series or parallel connection, WSF-DSSC could provide a special IV output in extremely narrow working environments or in those with unique, spatial shape requirements. That is quite useful for fast-developing portable mini electronic equipments based on COMS, which often requires only small current. It is worth proposing that due to the woven features of the WSF-DSSC, they

could be woven into modules with special shapes such as annular-like, rope-like, reticulate-like, branch-like, bag-like, or clothing-like, in order to meet special requirements.

In summary, we have explored a type of WSF-DSSC that does not need TCO. Formed by two fiber-like electrodes twisting together, the entire cell is still flexible wire. The IV output of WSF-DSSC is not influenced by the incident angle of the light. By coating PPL on the counter electrode, local stress on certain parts between electrodes could be effectively relieved. The experiment indicated that the PTL structure ex-

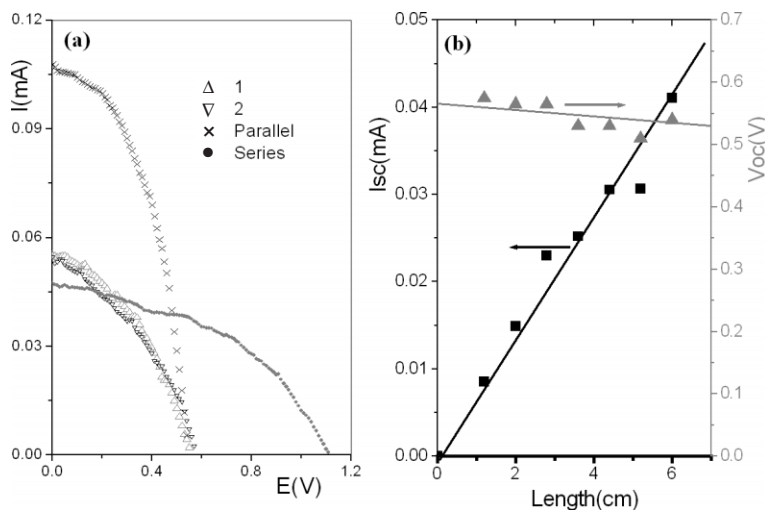


Figure 4. a) IV curves of Δ Cell 1; ∇ Cell 2; \bullet Cells connected in series; \times cells connected in parallel; b) ■ I_{sc} and ▲ V_{oc} of cells with different length.

erts a great influence on cell's performance. When the PTL was 3.5 μm thick, the V_{oc} , I_{sc} , and fill factor of a 5 cm WSF-DSSC were 610 mV, 0.06 mA, and 0.38, respectively. Within our experiment's range, the cell's I_{sc} is in direct proportion to the length. Special voltage and current can be achieved by a simple series or parallel connection of cells. Cell performance could be enhanced through further optimization of the PPL materials and the PTL structure.

Experimental

The working electrode was prepared according to the patent [15]. The TiO_2 colloid was prepared according to the second method in the literature [2]. After being degreased with acetone, the stainless steel wire (0.1 mm) was sintered for 15 min in 500 °C air. Afterward, it was dipped in an ethanol solution of titanium isopropoxide (ACORS) (0.01 M)/acetyl acetone (0.02 M) for 30 s, taken out, and then sintered at 500 °C for 15 min; this process was repeated thrice. The diluted TiO_2 colloid was then homogeneously sprayed on the surface of the wire under the illumination of an infrared lamp and was sintered for 30 min at 500 °C. The thickness of the porous TiO_2 layer (PTL) can be controlled by the TiO_2 colloid's concentration and spray time. The sintered TiO_2 electrode was cooled down to 100 °C in air and then soaked in an ethanol solution of 3×10^{-4} M N3 (*cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)) (as prepared according to the method in the literature [2]). Before testing, it was treated with 4-*tert*-butylpyridine (Aldrich) as indicated in the literature [2].

The counter-electrode was 99.9 % Pt wire (diameter = 0.1 mm). The PPL was also prepared by spraying, and the spraying solution was *N,N*-dimethylformamide (DMF) solution of poly(vinylidene fluoride) (PVDF).

The working electrodes were twisted with the counter electrode, soaked in the electrolyte for 2–3 s, and then were taken out for testing. Because of the capillary force, the electrolyte could stay for quite a long time in-between two electrodes even without any package. The electrolyte was a solution contained 0.5 M LiI (Aldrich) and 0.05 M I_2

(AR) 3-methyl-2-oxazolidinone (Aldrich)/ CH_3CN (1:9). Without special notes, the effective length of the cell in this thesis was 5 cm. The simulated solar light source was YSS-50A (Yamashita DESO), and the light intensity was 100 mW cm^{-2} .

The electrode's morphology was observed via scanning electron microscopy (SEM) (S570 Hitachi).

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