Fibrous flexible solid-type dye-sensitized solar cells without transparent conducting oxide

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We have explored a type of all-solid fibrous flexible dye-sensitized solar cells without transparent conducting oxide based on a CuI electrolyte. The working electrode's substrate is a metal wire. Cu wire counterelectrode is twisted with the dye-sensitized and CuI-coated working electrode. The cell's apparent diameter is about 150 μm. The cell's current-voltage output depends little on the incident angle of light. A 4-cm-long fibrous cell's open-circuit voltage and short-circuit current generate 304 mV and 0.032 mA, respectively. The interfacial interaction between the two electrodes has a significant influence on the inner charge transfer of the cell. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2891051]

As a type of low-cost, environment-friendly but highly efficient photovoltaic device, dye-sensitized solar cells (DSSCs) are seen as potential photovoltaic devices. Since 1987, many efforts have been devoted on DSSC.[1–5] The efficiency ($\eta_{AM1.5}$) of liquid DSSCs using fluorine-doped tin oxide glass as the substrate of working electrode (WE) has exceeded.[6,7] In order to improve the stability and the packaging ability, all-solid DSSCs based on solid electrolytes, such as CuX (X=I$^-$, SCN$^-$, ...) and organic semiconductors, have also been developed.[8] To further facilitate product design, transportation, installation, and application, the flexible DSSC, especially those of transparent conducting Oxide (TCO) free type, has become a challenge. Current studies on flexible DSSC focus mainly on the polymer/ITO (indium-tin oxide) substrate.[9–12] To avoid its disadvantages such as poor heat resistance, Kang *et al.*[13] developed a type of DSSC using stainless steel foil as the WE's substrate, the $\eta_{AM1.5}$ of which reached 4.2% (1000 W/m^2). Since the WE was opaque, they used transparent Pt-coated poly(ethylene terephthalate)/ITO as the counterelectrode (CE). Our team had replaced the traditional TCO materials with heat-resistant conducting mesh and assembled a type of TCO-free flexible liquid DSSCs.[14] A type of fibrous TCO-free flexible liquid-type DSSCs had also been assembled based on the metal wire.[15]

Compared with the liquid-type DSSC, the all-solid DSSC is more stable and easier for packaging. To expand the DSSC's flexibility to a higher dimension, we produced a type of fibrous WE based on stainless steel wire and assembled a type of all-solid flexible fibrous DSSC (ASFF-DSSC) using Cu wire as the CE and CuI as the electrolyte. As for the ASFF-DSSC, not only the stability and packaging ability are improved but the cost of production is also low, as it has a simple structure and abundant raw supplies.

The fibrous conducting substrate used was a 100 μm stainless steel wire. The 50 μm wire was also compared, as is in Fig. 2(b). After being cleansed and degreased in acetone, the wire was sintered at 500 °C in air for 15 min. A dense TiO_2 layer was then prepared using the aerosol synthesis method as specified in the literature.[16] After that, to form a 4-μm-thick porous TiO_2 layer, the TiO_2 colloid was homogeneously and repeatedly coated on the dense-TiO_2-layer-precoated fiber and was then sintered at 500 °C for 30 min. The TiO_2 colloid was prepared in accordance with the second method in the literature.[2] The thickness could be controlled by the concentration of the colloid and the number of coating. The TiO_2 electrode, after being sintered, was cooled to about 100 °C. The TiO_2 electrode was then immersed in an ethanol solution of $3\times10^{-4}M$ N3 Dye [*cis*-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)] (prepared as specified in the literature)[2] for 12 h. The surface of the dye-sensitized fibrous WE was then coated with CuI at 110 °C in a N_2-filled glovebox until the CuI formed a continuous phase. The dye-sensitized fibrous WE with CuI was allowed to thoroughly dry. The CuI/CH_3CN solution was prepared as specified in the literature.[8] The CEs were 0.05 mm Cu wires. The WE was evenly twisted with the CE. During the twisting, the component pressure normal to the twisting axis (f_p) was kept constant, and the screw pitch was 1.5 mm. (More fabrication details were given in supplemental information.)

For comparison, we also produced a DSSC based on a foil-type CE of 0.1 mm Cu foil. The assembly process are as follows: after the fibrous WE was fixed onto the surface of the Cu foil, it was then heated to 110 °C; drop by drop, CuI/CH_3CN solution is added until the gap between the two electrodes was filled with CuI.

The solar simulator used was YSS-50A (Yamashita DESO). Without special description, the light intensity was 1000 W/m^2. There was no mirror attached on the back side of the fibrous cell. The cell's morphology was observed via scanning electron microscopy (SEM) (S570 Hitachi).

The entire ASFF-DSSC was a very thin and flexible fiber. Figure 1(a) shows the optical photo of a cell. The entwined part of the WE and the CE is about 4 cm long. Figures 1(b)–1(d) show the cell's SEM images, from which we can see the entwined WE and CE. The cell's diameter, about 150 μm, is equivalent to the sum of the diameters of WE and CE. Meanwhile, it could be observed from Fig. 1(c) that there are still many defects in the CuI layer on the surface of

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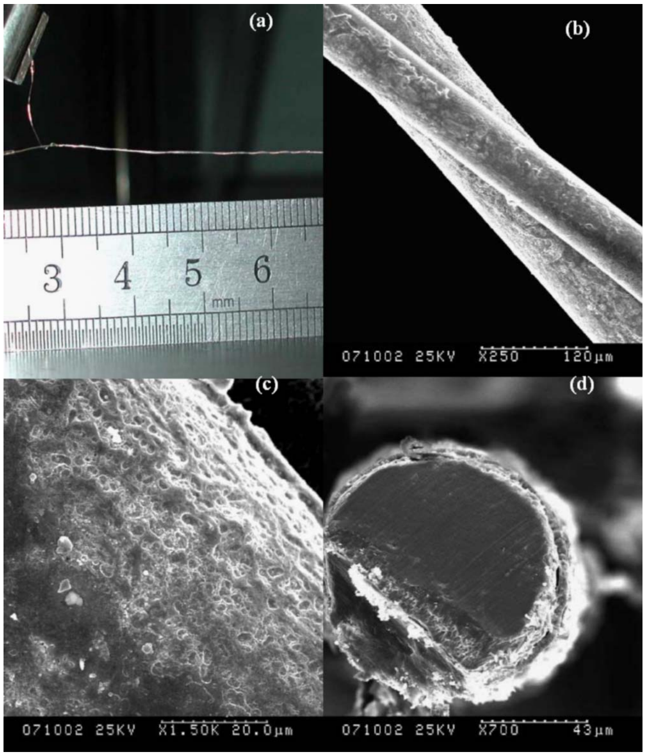

FIG. 1. (Color online) (a) Optical photo of an ASFF-DSSC. (b) SEM image of an ASFF-DSSC. [(c) and (d)] Top and sectional views of the fibrous WE.

the WE. This resulted from the nature of the solid electrolyte and the current on-wire coating technique. The cell would be improved if the carrier mobility, specifically along the electrode's surface, is enhanced.

The interfacial interaction of the electrodes greatly influenced the interfacial carrier transfer. While excessive interfacial pressure could increase the chance of electron-hole recombination, or even short circuit, very low interfacial pressure cannot ensure enough ohm contact. As shown in Fig. 2(a), the cells of different interfacial pressure states performed differently. When the interfacial pressure went too low, the open-circuit voltage (V_{oc}) produced was large, but the short-circuit current (I_{sc}) and fill factor (FF) of the cell were low. When the interfacial pressure is set too high, V_{oc} and I_{sc} would be both evidently reduced. The WE's diameter did not have any significant influence on the cell's performance compared to other factors, such as the electrode's interfacial interaction. As is shown in Fig. 2(b), after proper optimization, the I_{sc}-to-diameter ratio of cells with thinner WEs did not change significantly, and the V_{oc} was also similar.

Through preliminary optimization, a 4-cm-long ASFF-DSSC yielded a result of $V_{oc}=304$ mV, $I_{sc}=0.032$ mA, and FF=0.265 (AM1.5, 1000 W/m^2), as shown in curve (i) in Fig. 3(a). As for its special structure, the exact illumination area is hard to define. Assuming we set the cell's length at 4 cm and the width at 0.015 cm, the apparent photocurrent density is 0.53 mA/cm^2. Even without any packaging, the cell's max efficiency did not falter after it was stored in dry atmosphere for 500 h, as shown in curve iii in Fig. 3(a). Compared with the liquid-type fibrous DSSCs, the ASFF-DSSC's stability was obviously improved.

A solid-state DSSC on a Cu foil was assembled using the same electrolyte and fibrous WE. The cell's structure and the working curve are shown in Fig. 3. With current assembling techniques, due to better Ohm contact and less interfacial defects, a foil-type-CE cell obtained a preliminary result of $V_{oc}=388$ mV, $I_{sc}=0.069$ mA, and FF=0.469 under the same testing conditions. The preliminary study showed that on the electrode's interface of the fibrous DSSC, there are still many things to do in order to improve the efficiency.

Due to the symmetric twisting structure between electrodes in ASFF-DSSC, the cell's illumination state would still be the same whether the incident light came from any direction normal to the twisting axes. The fibrous cell's performance had lower dependence on the light's incident angle as compared to the foil-type-CE cell, as shown in Fig. 4(a). Moreover, by placing a mirror at the hind side of the fibrous cell to improve the illumination status on the hind side, the

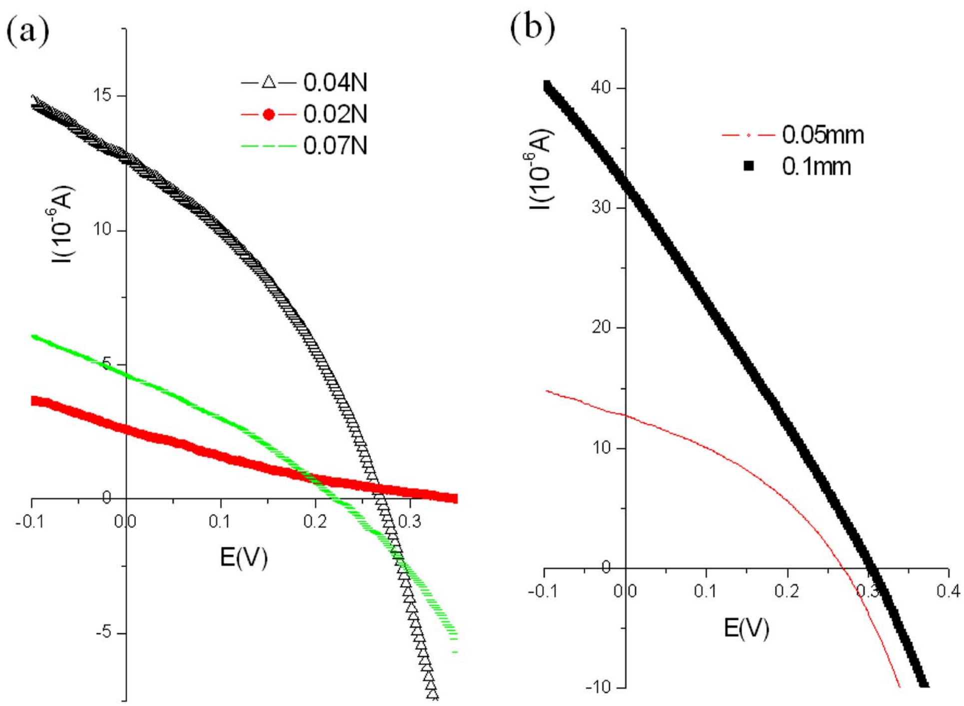

FIG. 2. (Color online) (a) *IV* performance of cells at different f_p (dash lines, 0.07 N; open triangle, 0.04 N; closed circle, 0.02 N); (b) *IV* performance of cells using WE of different diameters (dash lines 0.05 mm; closed square, 0.1 mm).

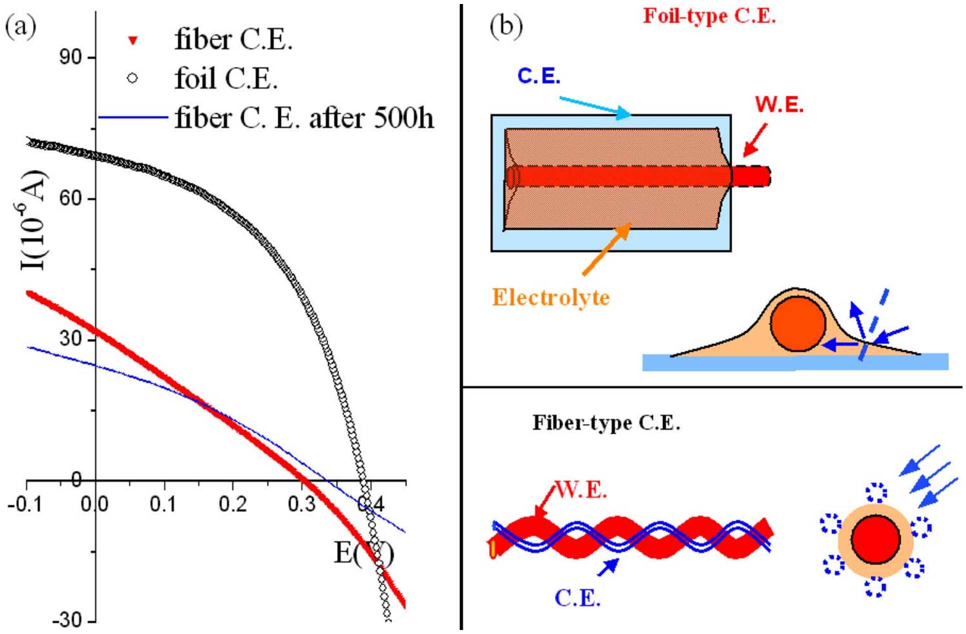

FIG. 3. (Color online) (a) *IV* performance of cells (i) using fiber-type CE (inverted closed triangle) and (ii) using foil-type CE (open circle). (iii) The *IV* performance of the ASFF-DSSC after storing in dry atmosphere for 500 h is also presented (solid line). (b) Structures of the two type of cells.

cell's I_{sc} improved by almost twice and the V_{oc} also increased. As shown in Fig. 4(b), the total output of the fibrous device, different from traditional sheet-type device, reflected the overall illumination from different directions in the environment. The cell's total output is equivalent to the shunt-wound output of cells in different directions. It could be a potential optoelectronic sensor for environmental testing.

In conclusion, we have explored a type of very cheap ITO-free flexible fibrous DSSC. Its WE is TiO_2- and CuI-coated conducting wire. The fibrous WE was twisted with Cu wire, and the cell's overall diameter was less than 0.15 mm. The interfacial interaction had a significant influence on the performance. Unlike the foil-type-CE cell, all wire-type cell's output is rarely influenced by the incident angle of light, but it reflects the overall illumination from different directions. A 4-cm-long ASFF-DSSC obtained a preliminary result of V_{oc}=304 mV and I_{sc}=0.032 mA. Even without any packaging, the cell's stability was relatively good. With further optimization of the materials and the device's structure, notable improvement in the cell's performance is expected. As the electronics industry develops, especially for portable and highly integrated microelectronic equipment, solar cells with higher degrees of freedom certainly have a promising future. Time will come when the idea of a wearable solar cell will be realized.

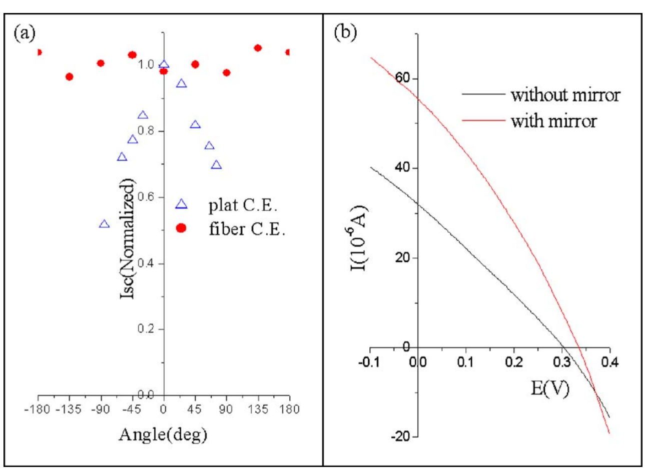

FIG. 4. (Color online) (a) I_{sc} vs incident-light angle of cells (i) using fiber-type CE (closed circle) and (ii) using foil-type CE (open triangel). (b) *IV* performance of an ASFF-DSSC with or without a reflecting mirror behind.

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