1. Introduction

Recently, fibers and textiles have been considered as promising platforms for low-cost flexible electronics and multifunctional fabrics, referred to electronic fibers (e-fibers), electronic textiles (e-textiles), or smart textiles. The one-dimensional (1D) structures such as fibers can stably work in both the bending and twisting states as well as in the other complex deformation states. In addition, the 1D structures can be weaved to form a large variety of complex, two-dimensional (2D) or three-dimensional (3D) patterns. Therefore, fiber- and textile-shaped energy harvesters such as photovoltaic, thermoelectric, and piezoelectric conversion devices are strongly required over a wide range of applications for smart textiles such as clothings, bags, curtains, carpets, tents, awnings, and shading elements [1–10].

Organic photovoltaic (OPV) cells, which can be fabricated by simple processing techniques, are being intensely studied because of their potential to enable the mass production of lightweight, flexible, and low-cost devices. Most of the attention has been focused on solution-processed polymer bulk-heterojunction (BHJ) cells [11]. Performance of OPV cells based on specially designed semiconducting polymers have led to power conversion efficiencies (PCEs) reaching about 10 % under air mass 1.5 global (AM 1.5 G) condition [12]. By using solution process, semiconductor polymers can also be coated to the various substrates including thin fibers and wires. However, producing of polymer-based fiber-shaped cells with precisely thickness-controlled functional layers by using solution process and stably waving of them into textiles are still challenging.
In the present study, we developed fiber- and textile-shaped organic photovoltaic cells for an energy harvester of smart textiles by using solution processing. The objectives of the present study are to fabricate (i) fiber-shaped cells by solution processing of all functional layers including transparent resin-coating layer under ambient conditions and (ii) fiber-based textiles by weaving of the coated photovoltaic fibers.

2. Experimental Section

2.1 Materials

Poly(3-hexylthiophene) (P3HT, regioregular electronic grade, Mw = 50-70 K) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, electronic grade, purity 99.9 %), and poly (3,4-ethylene - dioxythiophene): poly (styrenesulfonate) (PEDOT:PSS, Clevios PH 1000) were purchased from Rieke Materials, Sigma-Aldrich, and Heraeus respectively. 2-propanol (IPA, purity 99.7 %), zinc acetate dihydrate (ZnAc, purity 99.9 %), 2-methoxyethanol (purity 99.0 %), 2-aminoethanol (purity 99.9%), monochlorobenzene (MCB, purity 99.0%) and \(\text{O-dichlorobenzene (} \text{O-DCB, purity 98.0 %)},\) and ethylene glycol (EG, purity 99.5 %) were obtained from Wako Pure Chemical Industries. All reagents and solvents were used as received.

2.2 Fabrication of fiber- and textile-shaped photovoltaic cells

The structures of photovoltaic fibers are shown in Fig. 1 [10]. A stainless steel wire (Diameter: 0.127 mm, Fe:Cr:Ni = 70:19:11 in weight ratio, Type 304, Alfa Aesar) was used as primary electrode. The wire was washed with IPA at 80 °C for 10 min and completely dried by blowing N2. In the air, functional layers were dip coated at different coating speeds in order to control the film thickness of each layer [13]. An electron transport layer of zinc oxide (ZnO) was formed on the wire surface by the sol-gel method. The coating solution was prepared by dissolving ZnAc in 2-methoxyethanol and 2-aminoethanol. ZnO precursor layer was coated on the wire surface and then the coated wire was annealed at 250 °C for 60 min in an oven. A photoactive layer of P3HT and PCBM, which were commonly used materials for organic photovoltaic cells, was coated on the ZnO layer. The solution was prepared by dissolving P3HT:PCBM (= 2:1 in weight) in a mixture of MCB and O-DCB at room temperature. The active layer-coated wires were annealed at 145 °C for 15 min in an oven. After that, a transparent electrode layer of PEDOT:PSS was coated on the wire surface. The PEDOT:PSS solution with 6 vol% EG and 0.5 vol% fluorosurfactant (Zonyl FS-300, Fulka) was prepared. The cells were then annealed at 120 °C for 10 min in an oven. Thereafter, as secondary electrode to contact the PEDOT:PSS layer, Au wire (0.05 mm, Ametek) was twisted around the multi-layer coated wires by using a rotating machine. The fabricated photovoltaic fibers were cut into small pieces of 5 - 6 cm long. The fibers were dip-coated in an acrylate resin dispersion (OM-39 polymer, Soken Chemical & Engineering Co., Ltd.) bath for sealing. The coated layer was solidified in air for 15 min. The coated photovoltaic fibers were woven into polyethylene terephalate (PET) fabric by using a handloom (Fig. 2).

2.3 Characterization

Scanning electron microscope (SEM, KEYENCE VE-7800) was used to observe the surface morphology of the coated and uncoated wires, operated at acceleration voltages of 1.7 kV and 5.0 kV, respectively. Reflection spectra of ZnO crystals formed on the wire surface were determined by UV-VIS-NIR microspectrophotometer (JASCO MSV-5200) in the range from 300 to 700 nm. Cross-sectional morphology of the photovoltaic fibers was observed using a filed-emission scanning electron microscope (FE-SEM, JEOL JFM 7500 F), operated at acceleration voltage of 0.5 kV.

The current density-voltage (\(J-V\)) characteristics

![Fig. 1 Schematic structures of fiber-shaped photovoltaic cell (a) without and (b) with transparent resin coating.](image-url)
of the photovoltaic fibers and textiles were measured using a Keithley 2400 source meter unit in air. The cell performance of photovoltaic fibers employed an air AM 1.5 G solar simulator (Bunkoh-Keiki OTENTOSUN III) with an irradiation intensity of 100 mW/cm² (approximately over 400,000 lx). In addition, the cell performances were also measured with a white LED light at 5,000 lx (1.8 mW/cm²) irradiation. The irradiated area of the cells was determined by multiplying the length by the diameter of the fibers. Current density values were calculated based on the cell area.

3. Results and discussion

Fig. 3 shows the surface SEM images of stainless steel wire as the primary electrode before and after ZnO coating. The smooth surface is strongly required for the primary electrode in order to prevent electrical short circuit. Therefore, the wire should be attentively and sufficiently cleaned before ZnO coating. Surface SEM observation showed that defect-free ZnO-coated layer was formed after thermal annealing (Fig. 3b). In addition, the reflection spectra clearly indicated that the peak in the range of 330 – 400 nm appeared after ZnO-coating, which is ascribed to ZnO crystals (Fig. 4) [14]. These results suggested
that the crystalline ZnO layer was successfully coated on the wire surface and the layer thickness was approximately 50 nm determined by FE-SEM image (Fig. 5).

The photoactive P3HT:PCBM layer and hole-transport PEDOT:PSS layer were successively coated on the wire surface by meniscus coating. Their thicknesses are approximately 150 and 190 nm, respectively (Fig. 5). The coating technique utilized here achieved the considerably precise thickness controlling of polymer layers on the fibrous substrate sufficient for OPV device fabrication. The secondary electrode of Au wire was twisted around the coated wire to improve the electrically contact with the PEDOT:PSS surface at a controlled pitch of 3.8 mm (Fig. 6b). Digital microscopy observation demonstrated that the contact between PEDOT:PSS layer and Au wire is maintained after transparent resin coating. The thickness of the coating layer was approximately 80 μm determined by a digital micrograph (Fig. 6c).

The J-V curves of the fabricated photovoltaic fibers without and with transparent resin coating were measured under the standard sunlight irradiation at AM 1.5 G (the irradiation intensity, \( P_\text{in} = 100 \text{ mW/cm}^2 \)) and the indoor light irradiation at 5,000 lx LED lighting (\( P_\text{in} = 1.8 \text{ mW/cm}^2 \)). Typical J-V curves of the photovoltaic fiber are shown in Fig. 7.

The electrical power output and the power conversion efficiency (PCE) of the photovoltaic fibers were determined by the following equations:

\[
\text{Electrical power output (mW/cm}^2) = V_{oc}(V) \times J_{sc}(\text{mA/cm}^2) \times FF
\]

\[
PCE(\%) = \frac{V_{oc}(V) \times J_{sc}(\text{mA/cm}^2) \times FF}{P_{in}(\text{mW/cm}^2)} \times 100
\]

where \( V_{oc} \): open circuit voltage, \( J_{sc} \): short-circuit current density, and \( FF \): fill factor.

The performances of the photovoltaic fibers measured under standard AM 1.5 G irradiation and indoor lighting are summarized in Table 1. These results clearly indicates that sealing enhances the performance of photovoltaic fibers: \( J_{sc} \) increased from 9.1 and 16.6 mA/cm² and from 0.54 to 0.78 mA/cm² by transparent resin coating, resulting the electrical power outputs for the sealed fibers of 4.6 and 0.14 mW/cm² under the sunlight and indoor LED light irradiations, respectively. These power outputs are
sufficient for working small electronic devices such as wireless sensor nodes for Internet of Things (IoT) [15]. The coating processing greatly enhanced the photovoltaic performance. The possible reason is that the electrical contacts between the device surface and the secondary electrode Au wire was improved by transparent resin coating in addition to the mechanical stability. The electrical power output of the fiber-shaped polymer solar cells based on P3HT: PCBM under AM 1.5 G condition, 4.6 mW/cm², which corresponds to the PCE value of 4.6 %, compares to that of film-shaped ones. This value is higher than the reported PCEs for the solid-state fiber-shaped polymer solar cells (the best value ~ 3.8 % [6]). To the best of our knowledge, this is the highest PCE value for the solid-state fiber-shaped polymer solar cells [16].

Fig. 6 Photograph of photovoltaic fiber without sealing, and micrographs of photovoltaic fiber (b) without and (c) with sealing.

Fig. 7 J-V curves obtained from photovoltaic fibers without and with transparent resin coating under AM 1.5 G condition.

Table 1 Photovoltaic parameters obtained from J-V characteristics fiber-shaped photovoltaic cells with transparent resin coating under AM 1.5 G (100 mW/cm²) and 5,000 lx (1.8 mW/cm²) irradiation conditions.

| Irradiation intensity (mW/cm²) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm²) | FF | Electrical power output (mW/cm²) |
|-------------------------------|--------------|-------------------|----|---------------------------------|
| Without coating              | 100          | 0.54              | 9.1 | 0.43                            |
| With coating                  | 100          | 0.55              | 16.6 | 0.50                           |
| Without coating              | 1.8          | 0.37              | 0.54 | 0.32                           |
| With coating                  | 1.8          | 0.44              | 0.78 | 0.41                           |
|                               |              |                   |     | 2.1                            |
|                               |              |                   | 4.6 | 0.063                           |
|                               |              |                   |     | 0.14                           |
The coated photovoltaic fibers were stably woven into a polyethylene teraphtalate (PET) textile by using a handloom. The obtained photovoltaic textile showed not only excellent flexibility but also foldability (please see the Supporting Movie S1) and provide power under a white LED light irradiation.

### 4. Conclusions

In the present study, fiber-shaped organic photovoltaic cells with thickness-controlled functional layers were successfully fabricated by solution processing under ambient conditions. The transparent resin-coated photovoltaic fibers show an electrical power output up to 4.6 mW/cm² under the AM 1.5 G irradiation and 0.14 mW/cm² under LED lighting at 5,000 lx, and then were stably woven into a textile. The obtained photovoltaic textiles showed excellent flexibility and foldability in addition to power generation characteristics. These results have opened up the possibility of development of flexible, lightweight, low cost, and scalable fiber-based organic photovoltaic textiles for realization of self-powered smart textiles based on energy harvesting [17]. Our optics simulations clearly indicated that the appropriate thickness of transparent coating layer and the appropriate textile structure enhance the light absorption by single photovoltaic fiber and light trapping due to the interchange of light between the fibers, respectively [18]. We believe that it is possible to improve the performance by optimization of the coating layer of the photovoltaic fibers and/or the configurations of the photovoltaic textiles.

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