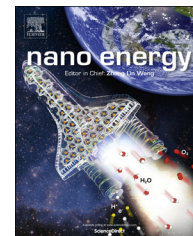




Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

Stitchable organic photovoltaic cells with textile electrodes



Seungwoo Lee^a, Younghoon Lee^a, Jongjin Park^{b,**},
Dukhyun Choi^{a,*}

^aDepartment of Mechanical Engineering, College of Engineering, Kyung Hee University, Seocheon-Dong, Giheung-Gu, Yongin-Si 446-701, Republic of Korea

^bSamsung Advanced Institute of Technology (SAIT), Mt. 14-1, Nongseo-Dong, Giheung-Gu, Yongin-Si, Gyeonggi-Do 446-712, Republic of Korea

Received 11 May 2014; received in revised form 15 June 2014; accepted 17 June 2014
Available online 17 July 2014

KEYWORDS

Stitchability;
Textile electrode;
Organic photovoltaic;
Hertzian theory;
Compatibility

Abstract

Organic photovoltaic cells (OPV) have been extensively studied and got great attention for a next-generation flexible power source due to their unique properties such as flexibility, light-weight, easy processability, cost-effectiveness, and being environmental friendly. Film-based OPVs however have a limitation for the applications in wearable products since they are not compatible with textile-based wearable products. In this study, we introduce a textile-based OPV as a stitchable power source. A large-area textile electrode can provide effective optical and mechanical characteristics for trapping incident light and high-durability. In order to define the power conversion efficiency (PCE) in the textile-based OPV, we suggest the theoretical approach to determine the contact area on a textile electrode by using Hertzian theory. It is demonstrated that our textile-based OPV can provide the enhanced short circuit current density, J_{sc} , of 13.11 mA cm^{-2} under 1 Sun condition, resulting in the PCE of about 1.8%. We expect that our textile-based OPV and theoretical approach might open the promising way to realize a compatible power source for wearable electronics.

© 2014 Elsevier Ltd. All rights reserved.

Introduction

Sustainable renewable energy systems that utilize the resources from nature such as solar, wind, and wave energies have attracted much attention due to the environmental issues and limited fossil fuels [1]. Among various renewable

*Corresponding author. Tel.: +82 31 201 3320; fax: +82 31 202 8106

**Corresponding author. Tel.: +82 31 280 6728; fax: +82 31 280 9308

E-mail addresses: jongjin00.park@samsung.com (J. Park),
dchoi@khu.ac.kr (D. Choi).

energies, photovoltaic cells are one of the cleanest, most applicable and promising alternative energies, using limitless sunlight [2,3]. Particularly, organic photovoltaic cells (OPV) have been extensively studied due to their unique properties such as flexibility, light weight, easy processability, cost effectiveness, and environmental friendliness [4-10]. These properties have competitive advantages over inorganic solar cells because they allow for the implementation of thin, light-weight, stretchable solar cells as a flexible power source [11-14]. They have found applications in the military, where soldiers need electricity for portable devices in remote areas [15]. In addition, there are many similar applications where personal, mobile wearable devices can be utilized [16]. However, most previous OPV studies have used flexible film-based cells, and they can be applied to wearable electronics such as smart watches and Google glasses. However, next-generation wearable electronics will be integrated with textile-based items such as clothes and bags, so that such film-based OPVs might be hard to be used to those wearable systems [17]. Therefore, it is crucial to design and develop textile-based power sources that are compatible with textile products.

Recently, fiber-based solar cells have been reported for wearable applications [18-22], but weaving of fiber-based solar cells remain a great challenge. Herein, this study introduces a textile-based OPV for a stitchable power source. A large-area textile electrode is prepared and characterized for optical and mechanical characteristics. Importantly, we suggest a theoretical approach to determine the contact area on textile electrode by using Hertzian theory in order to define the power conversion efficiency (PCE) on a textile-based OPV. Finally, we demonstrate an enhanced short circuit current density and determine the PCE of our textile-based OPV. We expect that our textile-based OPV and theoretical approaches might provide a promising avenue for finding power sources compatible with wearable electronics.

Experimental

Fabrication of OPV

First, an indium thin oxide (ITO) substrate with a sheet resistance of 200 Ω /square was prepared as a bottom electrode. A zinc oxide (ZnO) sol-gel solution was spin-coated

on the ITO and cured at 150 °C for 30 min for an electron transport layer. The sol-gel solution was prepared with zinc acetate dehydrate (99.999% metal basis) and ethanolamine dissolved in 2-methoxyethanol, where the concentration of zinc acetate was 0.5 M. The solution was mixed for 20 min at 80 °C prior to spin-coating. We applied a poly (3-hexylthiophene):[6,6]-phenyl C₆₁-butyric acid methyl ester fullerene derivative (P3HT:PCBM) mixture as a bulk heterojunction (BHJ) photoactive layer, where P3HT is used as an electron donor and PCBM is employed as an electron acceptor. P3HT and PCBM were dissolved in chlorobenzene (CB) at 65 °C for 18 h and blended at a ratio of 1:1. The P3HT:PCBM blend was spin-coated at 900 rpm for 60 s and then, thermal pre-annealing was performed at 120 °C for 10 min in a nitrogen atmosphere. The hole transport layer (molybdenum trioxide, MoO₃) was thermally evaporated with the thickness of 15 nm. Finally, a silver thin layer was deposited as a top electrode by thermal evaporation for a reference sample [23-29]. In order to create textile-based OPVs, we could apply a gold textile electrode instead of the silver layer.

Characterizations

The morphology characterization was obtained using a field emission scanning electron microscope (FE-SEM, Carl Zeiss LEO SUPRA 55). In order to confirm the light scattering effect, we used UV-spectrophotometer (Cary 5000, VARIAN) by using specular and diffuse reflectance modes. To verify the mechanical durability of our textile electrode, we measured the two-probe resistance under the repeating bending loads by using a bending machine (Z-tech). PECs of OPVs were measured using a Keithley 2400 source meter and a simulated AM 1.5 global solar irradiation with an incident power density of 100 mW/cm² using a solar simulator (HS-technologies).

Results and discussions

As mentioned above, film-based OPVs have low compatibility with textile products, and fiber-based OPVs remain to overcoming limit of fiber weaving. Our textile-based OPVs are highly compatible with textile products, thus proving the facile stitchability on textiles, as shown in Figure 1a. We could have applied our textile-based OPV to clothing

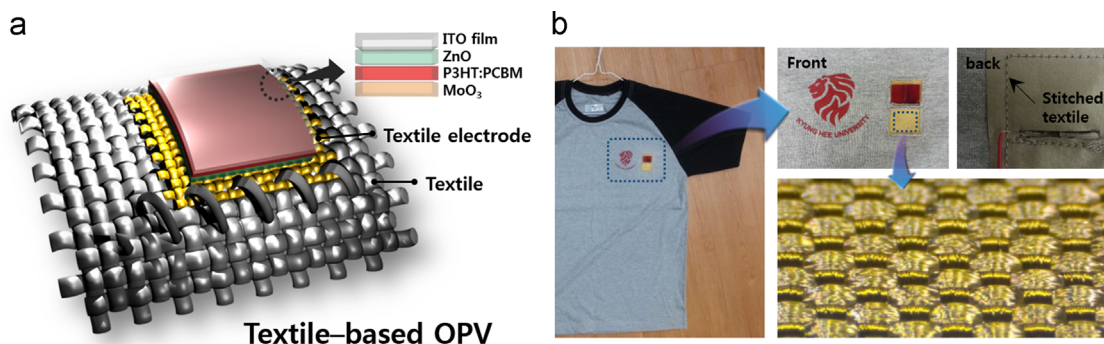


Figure 1 Stitchable OPV with a textile electrode. (a) Concept of a stitchable OPV on a textile electrode. (b) Photographs of the textile-based OPV integrated with clothing.

to demonstrate high compatibility (see Figure 1b). In brief, we cut the clothes and made a square hole. The textile electrode was then stitched to the clothes, and the wires can be connected at the backside of the clothes. As explained in Experimental section, an OPV without a silver electrode was prepared and integrated with the textile electrode as shown in Figure 1b. We expect that such a textile-based solar cell will be usually integrated on wears, bags, caps, tents, and so on. Of course, skin contact with the solar cell can be happened in cases, in which biocompatibility with skin should be investigated.

Figure 2a shows a large-area textile electrode over several of cm^2 that is produced by using electroless plating. As shown in the FE-SEM images of the textile electrode in Figure 2a, a bundle of fibers have been woven and showed not flat, but curved. The schematic image of Figure 2b shows the detail structure of the textile electrode. The single fiber has $10\ \mu\text{m}$ in a diameter where the woven fabric consists of fiber bundles. The single fiber is composed of several layers (see Figure 2b). Based on the polyethylene terephthalate (PET) fiber, nickel, copper, nickel, and gold were deposited by an electroless plating method which is the great way to obtain uniformly deposited metals with a complex geometry.

We investigated the optical characteristics of our textile electrode. As shown in FE-SEM and schematic images of Figure 2, the textile electrode has a curved morphology. Thus, we could expect high light scattering on the textile electrode, which is critically important to further absorb an incident light to enhance the performance of solar cells. We compared the optical behaviors of our textile electrode with those of a gold thin film electrode by measuring the reflectance in a UV-visible spectrophotometer. Specular reflection accessory (SRA) and diffuse reflection accessory (DRA) were used to analyze the optical reflectance of both specimens as shown in Figure 3a. The reflectance spectrum of the gold film in DRA was similar with the SRA result, as shown in the dot line of Figure 3b. On the other hand, the reflectance spectra of the textile electrode in DRA and SRA were critically different. This is attributed to the random

scattering of incident light on the curved textile electrode. Based on the SRA method (see the schematic of Figure 3a), the incident beam in SRA could not reach to the detector, thus resulting in almost zero reflection. As mentioned above, high light scattering enhances photo-absorption, thus resulting in high current density in solar cells. Based on the optical property of our textile electrode, it can be thus expected that our textile-based OPV might provide higher current density due to the enhanced photo-absorption.

To understand the mechanical durability of the textile electrode, we examined the electrical behavior of the textile electrode by mechanical deformation. We measured two-probe resistance of the textile electrode under repeating bending loads, as shown in Figure 4a.

We controlled the curvatures (κ) from $1.43\ \text{cm}^{-1}$ to $3.23\ \text{cm}^{-1}$ with the same bending speed of $3\ \text{cm/s}$. Two metal holders of the bending machine can measure the resistance of the textile electrode during bending. The initial distance between the holders was $50\ \text{mm}$, and the right holder moves to left side for operating. Figures 4b and 5c show the resistance profiles of the textile electrode under the repeating bending loads. By increasing the bending curvature, the electrical resistance of the textile electrode increased up to $12\ \Omega$, but it was still reversible to the original conditions. Thus, it can be seen that the textile electrode is quite durable and reliable under mechanical deformations.

In order to determine the PCE of solar cells, we should define the active area of the cell. In a textile-based OPV, the curved surface of textiles causes a difficulty to determine the real active area in the cell. Here, we suggest how to define the active area on the textile electrode based on Hertzian theory which can provide the contact area between two solid materials in contact. As shown in the enlarged schematic of Figure 5a, the active area in the textile-based OPV can be defined by obtaining the contact area between the curved textile electrode and the flat part of the cell including ITO/ZnO/P3HT:PCBM/MoO₃. In the Hertzian theory, some simplifying assumptions were made

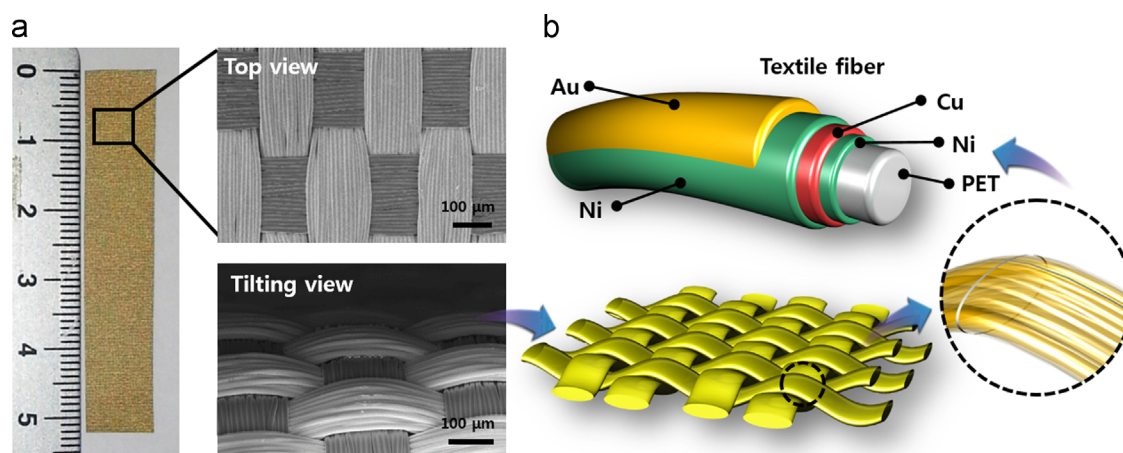


Figure 2 Detail configurations of the large-area textile electrode. (a) Large-area textile electrode over the size of $5\ \text{cm}^2$. FE-SEM images of the textile electrode with fiber bundles of curved surface. (b) The schematic images for the detail structure of the textile electrode.

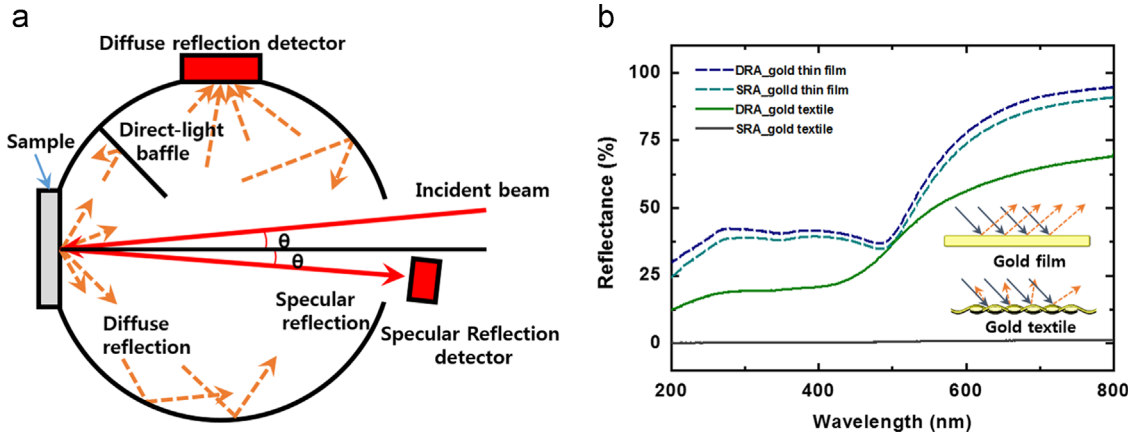


Figure 3 Optical characterizations of a textile electrode. (a) Schematic configurations for DRA and SRA modes. (b) Reflectance data of a gold thin film and a gold textile in the visible region.

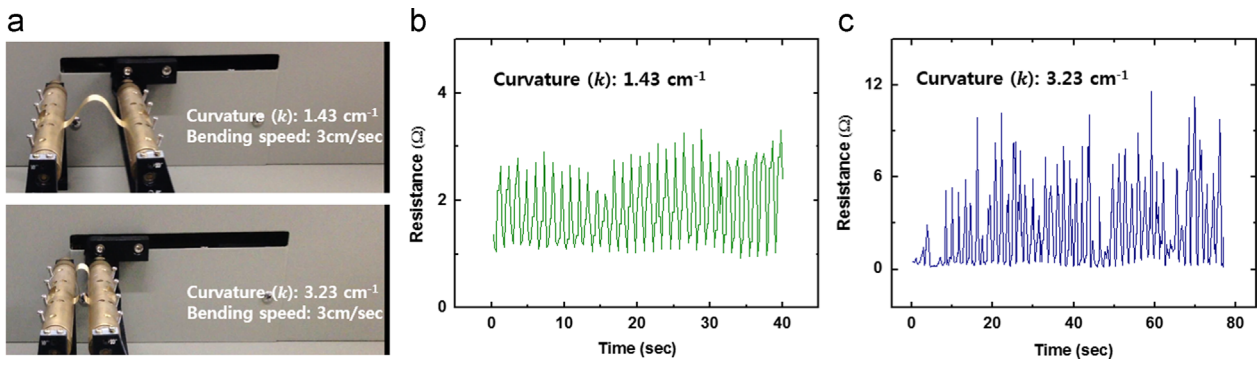


Figure 4 Mechanical durability of the textile electrode. (a) Photographs of the bending testing for different curvatures. (b, c) Two-probe resistance under the bending curvatures of 1.43 cm⁻¹ and 3.23 cm⁻¹.

and are summarized as follows; (a) surfaces are continuous and non-conforming (i.e. the initial contact is a point or a line) (b) strains are small (c) solids are elastic (d) surfaces are frictionless [30]. These assumptions imply that $a \ll R^*$, where a is the contact radius and R^* is the effective radius of curvature of the two solids. The effective radius (R^*) is defined by the radii (R_a and R_b) of curvature of the two solids as follows:

$$\frac{1}{R^*} = \frac{1}{R_a} + \frac{1}{R_b} \quad (1)$$

Based on the FE-SEM images in Figure 5b, we assume that the fiber bundle at the local position on the textile electrode can be considered as an ellipsoid solid with two different radii (R_1 and R_2). When the geometry of an ellipsoid ($R_1=160 \mu\text{m}$ and $R_2=420 \mu\text{m}$) in contact with a flat surface ($R \rightarrow \infty$) is considered, the effective radii, R^* and R^{**} , become R_1 and R_2 , respectively. In a similar manner, the effective modulus of elasticity can also be defined by the Young's modulus ($E_1=E_{\text{Au}}=78 \text{ GPa}$ and $E_2=E_{\text{MoO}}=40 \text{ GPa}$) of elasticity and Poisson's ratio ($\nu_{\text{Au}}=0.44$ and $\nu_{\text{MoO}}=0.2$) of the individual solids as follows:

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \quad (2)$$

The Hertzian theory assumes that only normal stress exists, i.e. the shear stress at the contact is zero. Under these conditions, the contact radius, a , is given by the

following expression;

$$a_1^3 = \frac{3PR^*}{4E^*}, \quad a_2^3 = \frac{3PR^{**}}{4E^*} \quad (3)$$

where P is a applied normal load at the contact position. As shown in Figure 5(c), the fiber bundles at the high points (see square dot) on the textile electrode make contacts, while those at the low points (circular dot) are not in contact. In the total area of 20 mm² in our textile-based OPV, the contact points (N) thus were 292. As a normal load, we applied a glass with the mass of about 200 g on the textile-based OPV. Based on the force equilibrium, we used the applied load of 200 g/N at each local contact position. As a result, we calculated the contact radii of $a_1=3.067 \mu\text{m}$ and $a_2=4.231 \mu\text{m}$ by using Eq. (3). Thus, the active area in the textile-based OPV was determined to be 40.8 μm² by the following expression:

$$A = N(\pi a_1 a_2) \quad (4)$$

Finally, we determine the PCE of our textile-based OPV and compared with a typical OPV with a silver top electrode. We could determine short circuit current density (J_{sc}) of our textile-based OPV based on the contact area calculated by the Eq. (3). Figure 6 compares the J - V curves of the textile-based OPV and a typical OPV. The typical OPV demonstrated a V_{oc} of $\sim 0.56 \text{ V}$, a FF of $\sim 44\%$, and a J_{sc} of $\sim 11.9 \text{ mA/cm}^2$. Therefore, the overall efficiency was 2.97%. On the other hand, the textile-based OPV had a V_{oc} of $\sim 0.57 \text{ V}$, a FF of 24%, and a J_{sc} of 13.11 mA/cm², resulting in the PCE of 1.79%.

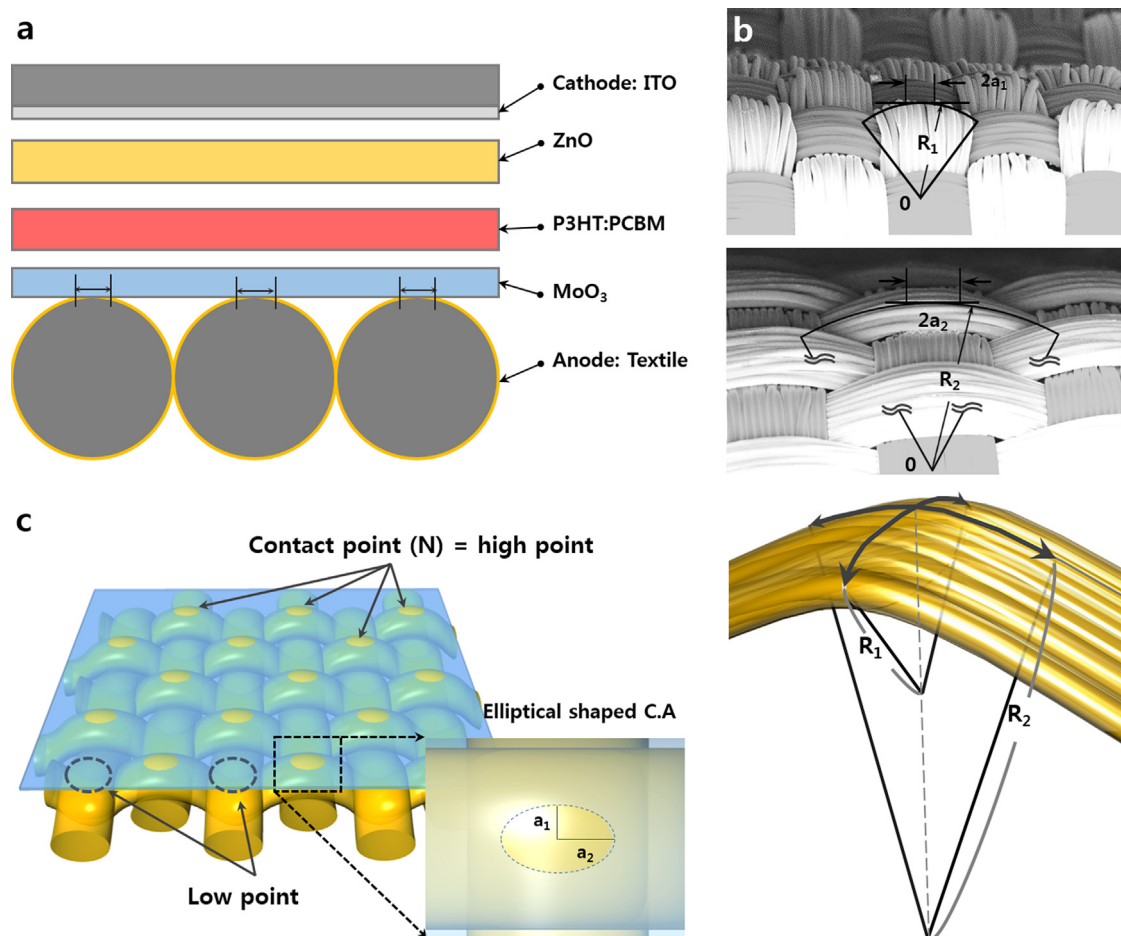


Figure 5 Suggested theoretical approach for contact area on the textile electrode. (a) Configuration of textile-based OPV; (b) FE-SEM and schematic images to define the contact area on a textile with the two radii (R_1 and R_2) of curvature. (c) Contact area on the textile electrode where higher points make contact, but lower points are not in contact. Furthermore, the contact is in an ellipsoid shape due to the curvatures of fiber bundle at each contact position.

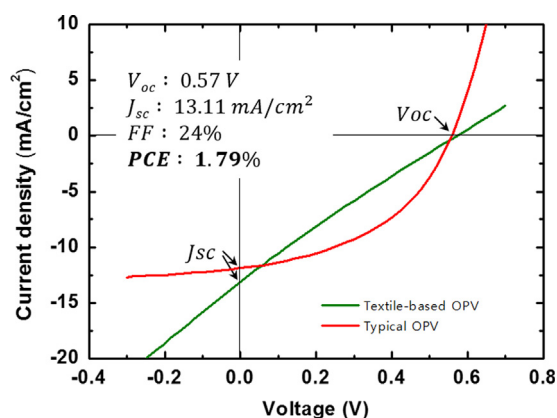


Figure 6 J - V curves of the textile-based OPV (green line) and the typical OPV (red line) under 1 Sun illumination.

Even though the PCE of our textile-based OPV decreased due to the weak physical contact (i.e. low FF), the enhanced short circuit current could be obtained. In detail, the open circuit voltages (V_{oc}) from textile-based OPV and typical OPV were almost same since a open circuit voltage in OPV is determined by the difference between the HOMO level of the donor and

the LUMO level of the acceptor. However, the fill factor (FF) of the textile-based OPV showed much less than that of the typical OPV. Generally, FF loss occurs when the series resistance increases in the cell. Of course, the other factors for FF loss can be considered like decreasing of shunt resistance. Our textile-based OPV is integrated with physical contacts, where the contact is unstable and has many air gaps, causing a high series resistance. Thus, FF was very low. We are under investigating for the enhancing the FF by improving the contact on the textile electrode. Interestingly, the J_{sc} ($13.11 \text{ mA}/\text{cm}^2$) from our textile-based OPV showed higher than that ($11.9 \text{ mA}/\text{cm}^2$) of typical OPV. This is because our textile electrode morphology could provide higher light scattering, as demonstrated in Figure 3b. The higher light scattering on the textile electrode can improve the photo-current density by confinement of the incident light, thus capturing more photons in the photo-absorption layer. As a result, we could obtain enhanced J_{sc} on our textile-based OPV.

Conclusion

In summary, we have successfully demonstrated a stitchable textile-based OPV. The textile electrode can be prepared at

a large-scale over several tens of cm^2 , and provided a high light trapping effect and high durability. Based on Hertzian theory, we proposed a way to determine the contact area in textile-based OPVs. Thus, our textile-based OPV showed the enhanced short circuit current density of $13.11 \text{ mA}/\text{cm}^2$, which is higher than that of a typical OPV, and the corresponding PCE reached to about 1.8%. Our design and theoretical approach might open the way to the creation of effective textile solar cells for next-generation wearable electronics.

Acknowledgments

This work was financially supported by the Energy International Collaboration Research & Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) funded by the Ministry of Knowledge Economy (MKE) (2011-8520010050), and by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2013R1A1A2063798).

Reference

- [1] L. Li, T. Zhai, Y. Bando, D. Golberg, *Nano Energy* 1 (2012) 91-106.
- [2] T. Song, S. Lee, B. Sun, *Nano Energy* 1 (2012) 654-673.
- [3] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science* 270 (1995) 1789-1791.
- [4] A.C. Mayer, S.R. Scully, B.E. Hardin, M.W. Rowell, M. D. McGehee, *Mater. Today* 10 (2007) 28-33.
- [5] S. Gunes, H. Neugebauer, N.S. Sariciftci, *Chem. Rev.* 107 (2007) 1324-1338.
- [6] K.M. Coakley, M.D. McGehee, *Chem. Mater.* 16 (2004) 4533-4542.
- [7] S. Kang, Y. Noh, S. Na, H. Kim, *Sol. Energy Mater. Sol. Cells* 122 (2014) 152-157.
- [8] D. Angmo, M. Hosel, F.C. Krebs, *Sol. Energy Mater. Sol. Cells* 107 (2012) 329-336.
- [9] J.K. Hyun, C. Ahn, H. Kang, H.J. Kim, J. Park, K. Kim, C. W. Ahn, B.J. Kim, S. Jeon, *Small* 9 (2013) 369-374.
- [10] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* 4 (2005) 864-868.
- [11] M. Kaltenbrunner, M.S. White, E.D. Glowacki, T. Sekitani, T. Someya, N.S. Sariciftci, S. Bauer, *Nat. Commun.* 3 (2012) 770.
- [12] D.J. Lipomi, B.C. Tee, M. Vosgueritchian, Z. Bao, *Adv. Mater.* 23 (2011) 1771-1775.
- [13] V. Yong, J.M. Tour, *Small* 6 (2010) 313-318.
- [14] J. Lee, J. Wu, M. Shi, J. Yoon, S. Park, M. Li, Z. Liu, Y. Huang, J.A. Roger, *Adv. Mater.* 23 (2011) 986-991.
- [15] D.J. Lipomi, Z. Bao, *Energy Environ. Sci.* 4 (2011) 3314-3328.
- [16] L. Hu, Y. Cui, *Energy Environ. Sci.* 5 (2012) 6423-6435.
- [17] Y.H. Lee, J.S. Kim, N.I. Lee, H.J. Kim, S. Choi, J. Seo, S. Jeon, T.S. Kim, J.Y. Lee, J.W. Choi, *Nano Lett.* 11 (2013) 5753-5761.
- [18] L. Zhang, L. Song, Q. Tian, X. Kuang, J. Hu, J. Liu, J. Yang, Z. Chen, *Nano Energy* 1 (2012) 769-776.
- [19] M.J. Uddin, T. Dickens, J. Yan, R. Chirayath, D.O. Olawale, O. I. Okoli, *Sol. Energy Mater. Sol. Cells* 108 (2013) 65-69.
- [20] S. Hou, Z. Lv, H. Wu, X. Cai, Z. ChuYiligumaD. Zou, *J. Mater. Chem.* 22 (2012) 6549-6552.
- [21] M.R. Lee, R.D. Eckert, K. Forberich, G. Dennler, C.J. Brabec, R.A. Gaudiana, *Science* 324 (2009) 232-235.
- [22] Z. Liu, M. Misra, *ACS Nano* 4 (2010) 2196-2200.
- [23] D. Zou, Z. Lv, X. Cai, S. Hou, *Nano Energy* 1 (2012) 273-281.
- [24] N. Sekine, C. Chou, W.L. Kwan, Y. Yang, *Org. Electron.* 10 (2009) 1473-1477.
- [25] L. Chen, Z. Hong, G. Li, Y. Yang, *Adv. Mater.* 21 (2009) 1434-1449.
- [26] G. Li, C. Chu, V. Shrotriya, J. Huang, Y. Yang, *Appl. Phys. Lett.* 88 (2006) (253503-253503-3).
- [27] S. Ihn, K. Shin, M. Jin, X. Bulliard, S. Yun, Y. Suk Choi, Y. Kim, J. Park, M. Sim, M. Kim, K. Cho, T. Sang Kim, D. Choi, J. Choi, W. Choi, S. Kim, *Sol. Energy Mater. Sol. Cells* 95 (2011) 1610-1614.
- [28] S.K. Hau, H. Yip, N.S. Baek, J. Zou, K. O'Malley, A.K. Jen, *Appl. Phys. Lett.* 92 (2008) 253301.
- [29] J. Lan, Z. Liang, Y. Yang, F.S. Ohuchi, S.A. Jenekhe, G. Cao, *Nano Energy* 4 (2014) 140-149.
- [30] S. Liu, A. Peyronnel, Q.J. Wang, L.M. Keer, *Tribol. Lett.* 18 (2005) 505-511.



Seung Woo Lee received the degree of Master of Engineering from the Kyung Hee University of Korea in 2014. His current research is focused on the nanomaterials application for energy conversion.



Young Hoon Lee majors in Mechanical Engineering as an undergraduate in the Kyung Hee University of Korea since 2009 to present. He is interested in designing and constructing innovative structures accommodating nanomaterials and fabricating nanodevices for the purpose of energy harvesting.



Jong-Jin Park received his Ph.D. degree from Korea Advanced Institute of Science and Technology (KAIST) in 1999. From 2002 to present, he has worked for SAIT as a master of materials and device. Dr. Park's current research program is wearable devices for mobile healthcare using functional nanofibers. He has published over 50 articles and holds 260 patents.



Dukhyun Choi received his Ph.D. in Mechanical Engineering from Pohang University of Science and Technology (Postech) in 2006. From 2006 to 2008, he was a postdoctoral fellow with Prof. Luke P. Lee at UC Berkeley. Dr. Choi moved to Samsung Advanced Institute of Technology (SAIT) as a research staff. Since 2010, he is a Professor in Department of Mechanical Engineering at Kyung Hee University. His research interests include Energy Harvester, Plasmonics, Hybrid Photovoltaics, Flexible Electronics, and Water Splitting. Details can be found at: <http://dchoi.khu.ac.kr>.