SCIENTIFIC REPORTS

OPEN

SUBJECT AREAS:
SOLAR CELLS
DESIGN, SYNTHESIS AND PROCESSING

Received
14 March 2014

Accepted
27 May 2014

Published
24 June 2014

Correspondence and requests for materials should be addressed to S.I.C. (sicha@keri.re.kr)

Highly Flexible Dye-sensitized Solar Cells Produced by Sewing Textile Electrodes on Cloth

Min Ju Yun, Seung I. Cha, Seon Hee Seo & Dong Y. Lee

Nano Hybrid Technology Research Center, Creative and Fundamental Research Division, Korea Electrotechnology Research Institute.

Textile forms of solar cells possess special advantages over other types of solar cells, including their light weight, high flexibility, and mechanical robustness. Recent demand for wearable devices has promoted interest in the development of high-efficiency textile-based solar cells for energy suppliers. However, the weaving process occurs under high-friction, high-tension conditions that are not conducive to coated solar-cell active layers or electrodes deposited on the wire or strings. Therefore, a new approach is needed for the development of textile-based solar cells suitable for woven fabrics for wide-range application. In this report, we present a highly flexible, efficient DSSC, fabricated by sewing textile-structured electrodes onto casual fabrics such as cotton, silk, and felt, or paper, thereby forming core integrated DSSC structures with high energy-conversion efficiency (∼5.8%). The fabricated textile-based DSSC devices showed high flexibility and high performance under 4-mm radius of curvature over thousands of deformation cycles. Considering the vast number of textile types, our textile-based DSSC devices offer a huge range of applications, including transparent, stretchable, wearable devices.

The demand for lightweight, highly flexible or bendable solar cells has grown rapidly as the application of photovoltaic electric power generation has widened to encompass urban life in the form of building-integrated photovoltaics (BIPV) or electronics-integrated photovoltaics (EIPV)[1–5]. Until several years ago, most of the research effort had focused on techniques involving flexible plastic substrates onto which transparent conductive oxide (TCO) films were deposited[6–8]. However, TCO films can be easily fractured, resulting in a loss of conductivity due to their brittle nature. More recently, there has been a renewed interest in traditional material-based flexible solar cells, such as those associated with paper, string/fiber, and textiles[9–26].

Textile forms of solar cells possess special advantages over other types of solar cells, including their light weight, high flexibility, and mechanical robustness. Recent demand for wearable devices has promoted interest in the development of high-efficiency textile-based solar cells for energy suppliers. Based on these demands, several studies have investigated the fabrication of textile-based solar cells, using organic solar cells or dye-sensitized solar cells[18–24]. However, these research efforts were basically aimed at producing wires or strings of solar cells, ignoring their condition during the weaving process. Generally, the weaving process occurs under high-friction, high-tension conditions that are not conducive to coated solar-cell active layers or electrodes deposited on the wire or strings. Additionally, current research results can only produce very short (tens of centimeters) strings, far less than the length required for actual weaving or textile-based applications. Therefore, a new approach is needed for the development of textile-based solar cells suitable for woven fabrics for wide-range application.

Dye-sensitized solar cells (DSSCs) have attracted much interest, due to their low fabrication costs, relatively high, efficiency especially under weak illumination, and ability to incorporate the dye color employed[1–5]. In terms of textile solar cells, DSSCs offer several advantages, including spatial separation of the photoanode and counter electrode via electrolyte insertion, which minimizes the possibility of a short circuit. By combining this approach with the concept of core-integrated DSSCs for paper-based TCO-free DSSC[9], we propose a new prototype for textile-based solar cells using DSSCs.

In this report, we present a highly flexible, efficient DSSC, fabricated by sewing textile-structured electrodes onto casual fabrics such as cotton, silk, and felt, or paper, thereby forming core integrated DSSC structures. By carefully fabricating the woven electrodes, the sewing process, one of characteristics of textiles, can be applied to the fabrication of solar cells as well as to the process of weaving using a loom.

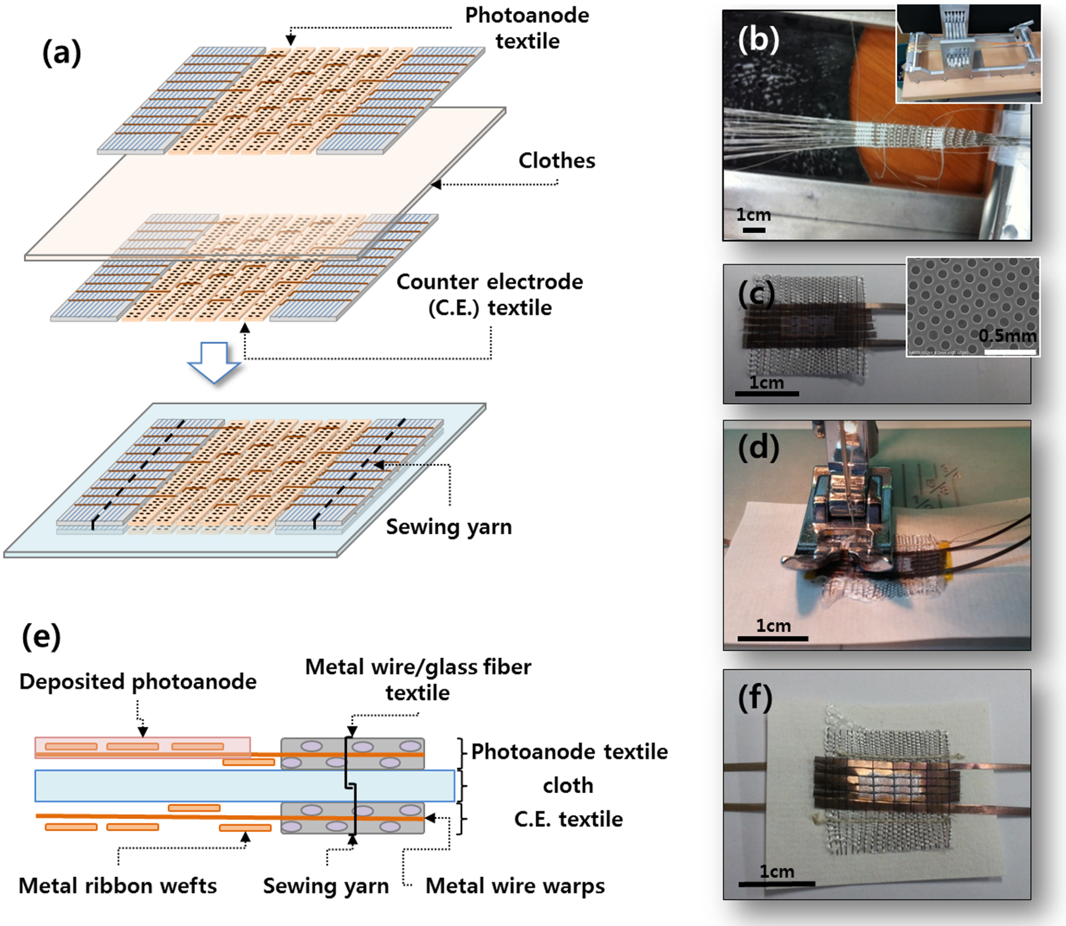

Figure 1 | (a) Schematic illustration of the fabrication concept for textile-based dye-sensitized solar cells (DSSCs) made by sewing textile electrodes onto cloth or paper. (b) Photograph of the loom (inset) used to weave the textile electrodes, and (c) a woven electrode. The inset shows an image of the stainless steel ribbon with periodic holes. (d) Photograph of the sewing process to attach the woven electrodes to Hanji, a Korean traditional paper. (e) Schematic illustration showing the cross-sectional structure of the textile-based DSSC prepared by sewing and (f) photograph of a core-integrated textile-based DSSC fabricated by sewing textile electrodes onto Hanji.

Results

The process used to create the textile-based flexible solar cells to be sewn onto cloth consisted of the following steps: weaving each electrode by loom, depositing the photoanode material (i.e., TiO_2) and the counter-electrode material (Pt), administering heat treatment, sewing to form the core-integrated DSSC device, and dye loading; these steps are shown in Fig. 1(a). The photoanode and counter-electrode textiles consisted of two parts: (1) a woven structure of stainless steel ribbon with periodic holes of 70 μm as the wefts and Ti wire of 100 μm as the wraps, and (2) the woven structure of glass fiber yarn as the wefts and Ti wire as the wraps (Fig. 1 (b) and (c)). The former (stainless steel/Ti wire) was used as the collector and as a substrate for the device; additionally, the later part provided mechanical support and robustness for sewing to the other textiles, as shown in Fig. 1(c). It should be noted that the textile electrodes consisted of heat-resistant materials, such as metal and glass fibers. Therefore, each electrode can be heat treated after the deposition of the TiO_2 porous film and Pt, which is an important factor for high-efficiency DSSCs.

The photoanode and counter-electrode textiles were woven using a 3 : 1 twill structure, providing relatively high flexibility and a flat woven surface. (See Supporting Information Fig. S1 for schematics of twill structured textile) Combined with stainless steel ribbon as the wefts, the textile structure photoanodes had quite flat structures compared with those expected in woven structures, as shown in Fig. 1(c). Therefore, the conventional doctor-blade process or screen-printing process was applied to deposit the electrode materials. The counter electrodes were prepared using two-step deposition of Pt. First, the Pt was deposited onto the counter-electrode textile using an electroplating method, and this was followed by the deposition of Pt-containing paste. The structure was then heat treated. Using this two-step deposition process, Pt thin flakes resembling flowers can be prepared (see Supporting Information Fig. S2 and S3 for images of the counter electrode and photoanode deposited). The prepared textile electrodes were assembled by sewing, placing each electrode on either side of the cloth, followed by electrolyte infiltration, as shown Fig. 1(d). The textile-structured electrodes were attached to the cloth (in this case, paper) using a sewing machine. As a result, core-integrated forms of DSSCs were fabricated; Figs. 1(e) and 1(f) show a cross-sectional schematics and a plane view, respectively. In the cross-sectional schematics, the DSSC prepared by the sewing process consisted of three layers, similar to conventional DSSCs; however, no TCO films or glass plates were employed, which is a particular feature of core-integrated DSSCs.

The photovoltaic performance of the textile-based DSSC sewn on Hanji, a Korean traditional paper, is shown in Fig. 2(a). The relationship between the current density and applied voltage shows a high short-circuit current (>17 mA cm^{-2}). However, the fill factor was low at only 0.37, which is the main limitation for energy conversion efficiency. The low fill factor can come from the low porosity of Hanji infiltrated with electrolyte and the evaporation of electrolyte on the surface of electrode due to lack of sealing during measure-

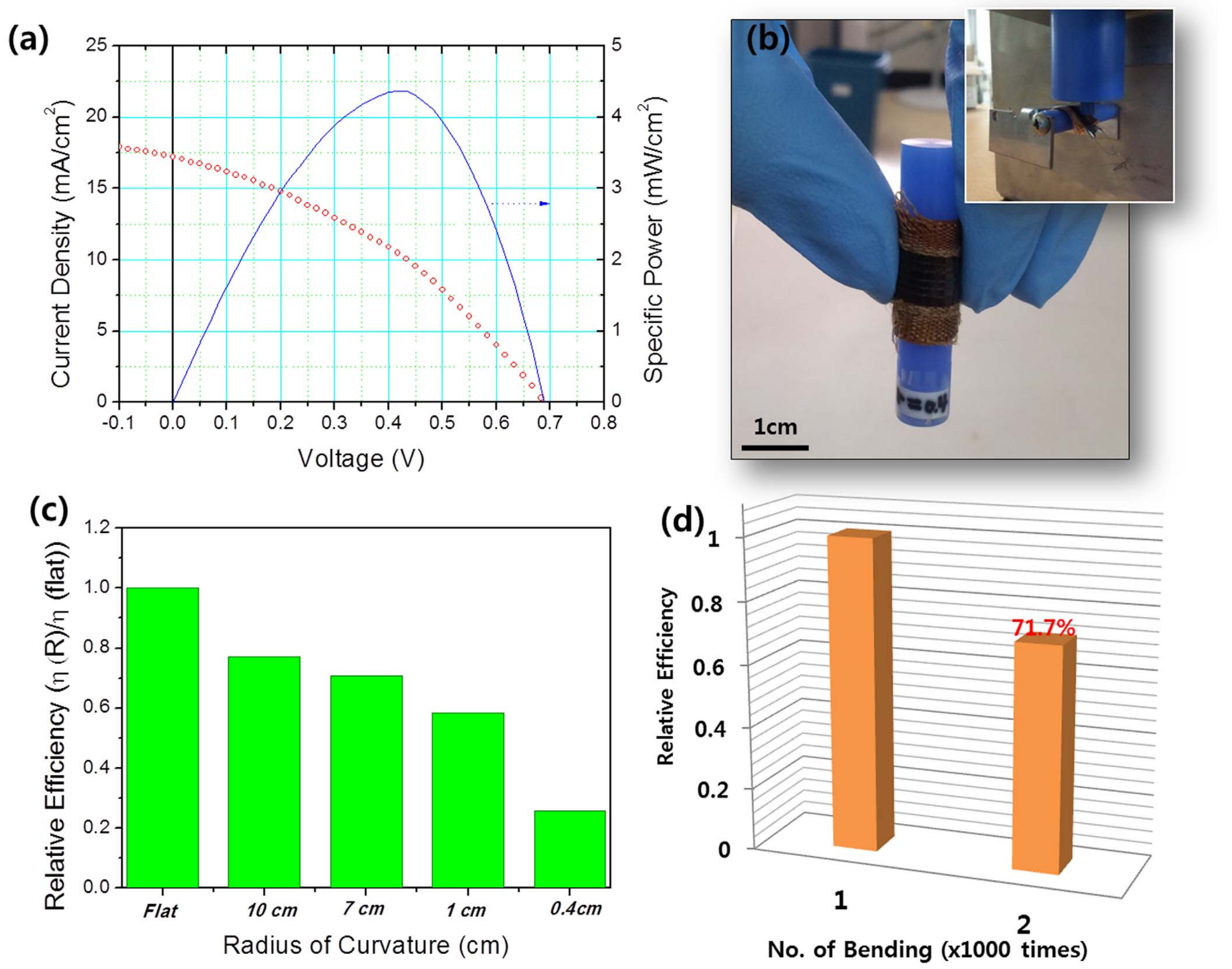

Figure 2 | (a) Relationship between current density and applied voltage (red circle) and specific power and applied voltage (blue line) of a textile-based DSSC prepared by sewing the woven electrode onto Hanji; measurements were obtained under 1-Sun, 1.5-AM conditions. (b) Photographs showing a textile-based DSSC wrapped around a rod with a 4-mm radius of curvature under cyclic bending deformation (inset). (c) Relative energy conversion efficiency of the flat-state textile-based DSSC and (d) relative efficiency after cyclical bending of 1000 and 2000 times.

ment. The overall efficiency under 1-Sun illumination was ~4.3% despite the high current density, with 5.3% corresponding to the maximum conversion efficiency observed.

The textile-based DSSC fabricated by sewing exhibited considerable bending ability, as shown in Fig. 2(b), where the prepared cell was wound around a rod of 0.4-cm radius of curvature. The cell underwent thousands of bending cycles of 90°. The photovoltaic performance under bending conditions was maintained at 80% of the flat cell value with bending to a 10-cm radius of curvature and 30% with a 4-mm radius of curvature, as shown in Fig. 2(c). Additionally, the photovoltaic performance remained over 70% of the initial value even after 1000 bending cycles over a 1-cm radius of curvature, as shown in Fig. 2(d). (See Supplementary Information Figure S5 and S6 for status of cell after repeated bending by pressing plunge).

The energy conversion efficiency of the textile-based DSSC sewn on cloth was affected by several factors; some of these factors, to the best of our knowledge, have yet to be considered for textile-based DSSCs. One such factor is the contact between the metal wires in the woven electrodes. If the contact between the metal wrap and weft is lost, then an electrical open circuit forms within the cell that acts as a recombination site during operation. Under these conditions, the energy conversion efficiency can be degraded considerably by loss of contact between the woven electrodes. It is not totally clear when the contact becomes lost; however, tension maintained during the weaving process, as well as the pattern of the weave, could have an effect on the electrical contact of the woven electrode.

Another factor that may affect photovoltaic performance of the textile-based DSSC is the cloth itself, which contains the electrolyte and plays the role of a spacer to prevent electrical short circuits from forming between the electrodes. Hanji has very few pores for diffusion within the electrolyte, as shown in Fig. 3(a), which induces a low fill factor during photovoltaic operations. To investigate the effect of cloth on photovoltaic performance, other types of cloth including cotton and silk (both in the form of gauze) were used for the textile-based DSSC as a spacer. The woven electrodes were attached to either side of the cotton and silk gauze using a sewing machine, as shown in Fig. 3(b); note that a mechanically robust core-integrated DSSC can be fabricated using these cloth types. This is particularly useful and meaningful with respect to the application of wearable devices for energy supply. The microscopic structures of the cotton and silk gauze are shown in Figs. 3(c) and 3(d). Compared with Hanji, the gauze offers more space for electrolyte filling and diffusion.

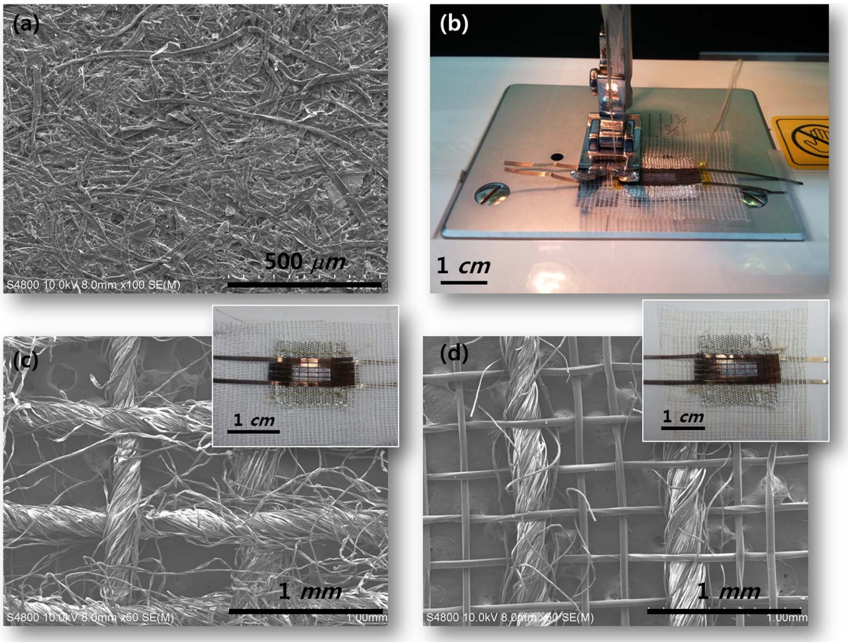

Figure 3 | (a) Scanning electron microscopy (SEM) image of the Hanji surface. (b) Photograph of the process of sewing woven electrodes onto silk gauze using a sewing machine. SEM images of the surface of (c) cotton gauze and (d) silk gauze. Inset shows prepared textile-based DSSCs using (c) cotton gauze and (d) silk gauze.

The open area of cotton gauze is measured as about 48%, while that of silk gauze is about 47%.

The effect of cloth type on photovoltaic performance indicates that the inserted cloth considerably affects energy conversion efficiency and the relationship between current density and applied voltage, as shown in Fig. 4(a). High current densities for the textile electrodes can be expected as a result of light reflection from the metal and enhanced photon harvesting[25,26]. The woven metal ribbon can reflect over 10% of incident light when it is oxidized. (See Figure S4 for light reflection from metal ribbon) It is also shown in wire-shaped solar cell that the light concentration by focusing light or luminescent concentrator could enhance energy conversion efficiency. In the case of cotton gauze, the current density decreased slightly, whereas the fill factor increased; hence, the energy conversion efficiency improved to 5%. When silk gauze is inserted between textile electrodes, the energy conversion efficiency was enhanced to 5.8%. For the champion cell, the efficiency is measured as nearly 7%; in this case, the current density increased to nearly 20 mA cm^{-2}, which is a high value, even for conventional sandwich-structured DSSCs, as summarized in Table 1. The enhancement observed with cotton gauze compared with Hanji can be explained in terms of the ease of diffusion in the electrolyte due to the large free space; the chemical status of the cotton and paper did not change significantly within the electrolyte under Fourier-transform infrared (FTIR) spectroscopy analysis, as shown in Fig. 3(b). However, in the case of the silk gauze, the electrolyte changed the chemical status of the yarn, as shown in Fig. 3(b), where absorption near 3200–3500 and 1600 cm^{-1} was observed after soaking the silk in the electrolyte for one day. The absorption that occurred was attributed to the formation of hydroxyl groups, amide groups, and aromatic groups, which exist in protein molecules. The electrolyte and spacer, chemically modified in the silk gauze, enhanced the energy conversion efficiency. Thus, the potential exists for further improvement beyond the results presented here.

Discussion

However, questions remain regarding the determination of energy conversion efficiency in these devices. High current densities for the textile electrodes can be expected as a result of light reflection from the metal and enhanced photon harvesting. For electrochemical impedance spectroscopy (EIS) results under open-circuit conditions, as shown in Figs. 3(c) and 3(d), the cloth type appeared to affect the resistance during electrode reactions. Nyquist plots indicated that this effect was smallest in cotton gauze and highest in silk gauze in short circuit condition. The Bode plots showed that the resistance was related to the reaction near the 10–100 Hz range, which may correspond to recombination in the photoanode. In this case, the recombination rate was related to the ionic concentration near the photoanode, which can be affected by diffusion and the initial ionic concentration. To find the optimum operating conditions for textile-based solar cells, further research on the cloth material is needed. It should be noted that in this study, we used conventional commercially available materials, including TiO_2 nanoparticle paste, common electrolytes, and a Pt counter electrode. This suggests the possibility for considerable improvement in photovoltaic performance of these structured DSSCs with suitable material optimization.

The woven pattern is another critical factor that may allow further improvement in performance. As mentioned earlier, the woven structure and the applied tension in the wraps and wefts determine the electrical contact within the woven electrodes. By considering various forms of textiles developed, semi-transparent electrodes or stretchable electrodes could be fabricated by proper selection of the weave pattern. In this sense, the preparation of DSSCs by sewing textile electrodes on various types of cloth provides vast potential for possible application.

In summary, highly bendable, mechanically robust DSSCs with high energy-conversion efficiency (~5.8%) can be fabricated by sewing textile electrodes prepared by loom weaving onto various types of cloth. The fabricated textile-based DSSC devices showed high flexibility and high performance under 4-mm radius of curvature over thousands of deformation cycles. Considering the vast number of textile types, our textile-based DSSC devices offer a huge range of applications, including transparent, stretchable, wearable devices.

Mothods

The etched mesh of 304 stainless steel (Tech-Etch MicroEtch®) and 50-μm-diameter Ti wire (iNexus) were used as the weft, and 100-μm-diameter Ti wire (iNexus) was

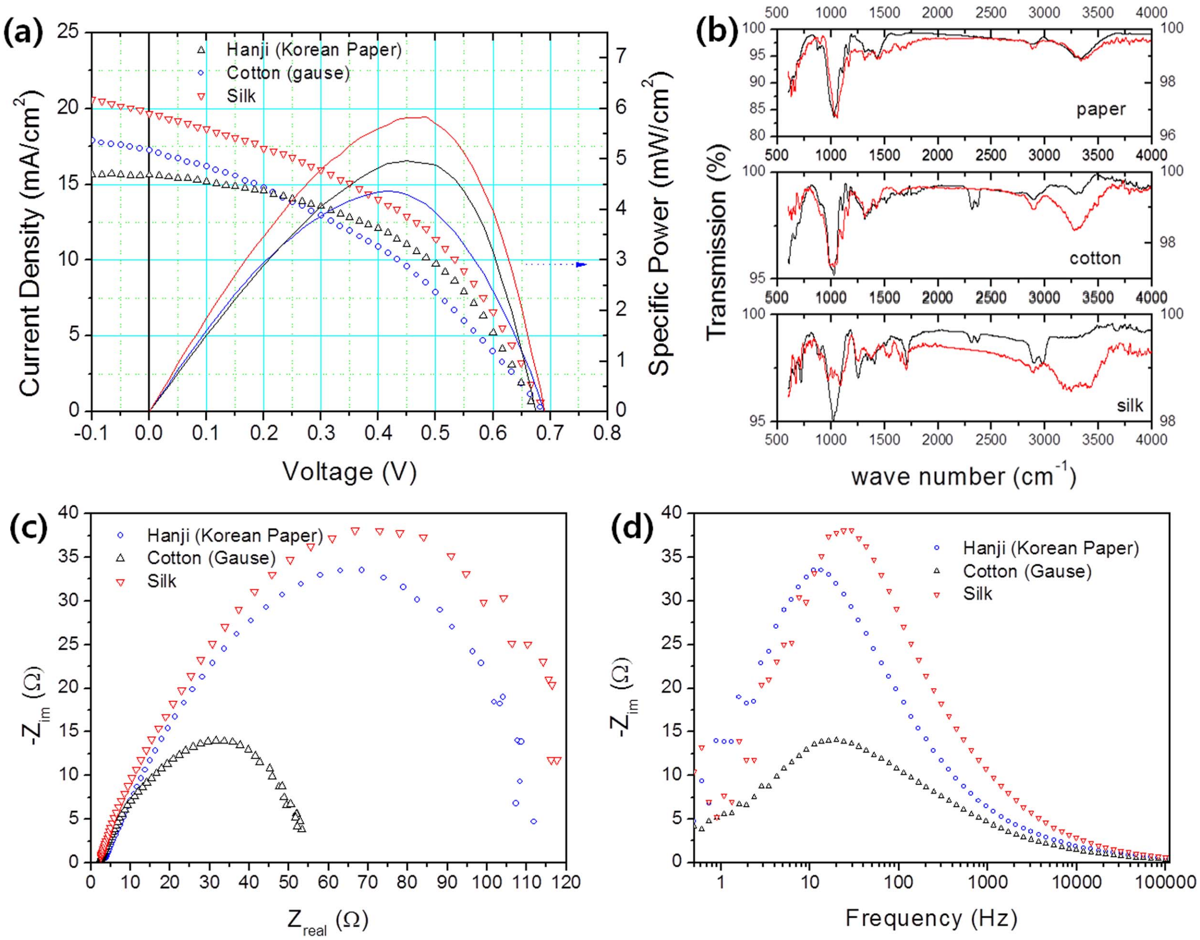

Figure 4 | (a) Relationship between current density, specific power, and applied voltage according to the cloth used: Hanji (blue circle), cotton gauze (black triangle), and silk gauze (red triangle). (b) Fourier-transform infrared (FTIR) spectra of Hanji, cotton gauze, and silk gauze before (black line) and after (red line) soaking in the electrolyte for one day. (c) Nyquist plot and (d) Bode plot of textile-based DSSCs using Hanji, cotton gauze, and silk gauze under open-circuit conditions and 1-Sun, 1.5-AM illumination.

used as the warp of the woven electrode. The sewn part of the electrode, a glass fiber (D450 1/2, Hyunmin Fiber), was used as weft. A Daesung Hi-tech loom (Daesung Hi-Tech Co., Ltd., Korea) was used for weaving.

The woven electrode was rinsed with acetone, ethanol, and deionized water by sonication and dried with nitrogen gas. After cleaning, the woven textile for the working electrode was heat treated at 480°C for 1 h in air for oxidation of the metal surface. After oxidation, a coating of TiO_2 paste containing 20-nm TiO_2 nanoparticles (EnB Korea) was applied using a 3M tape mask and the doctor blade method; the sample was then heat treated at 480°C for 1 h in air. For measurements, the active area size was 8 × 3 mm. The other woven electrode for the counter electrode was electroplated for deposition of Pt. Electrodeposition was carried out using an aqueous solution of 50 mM H_2PtCl_6 $6H_2O$ (Sigma Aldrich) at room temperature under 2 V direct current (DC) power for 5 min and then calcined at 180°C for 1 h. After calcination, Pt paste (Solaronix) was applied using the doctor blade method, followed by heat treatment at 400°C for 30 min.

The two electrodes and spacer were attached using a Toyota sewing machine. After sewing, the thickness of the devices is ranged from 0.7 mm to 0.8 mm. The prepared cell after sewing process was immersed in 0.3 mM ethanol solution of cis-di(thiocyanato)- N,N'-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammoniumcarboxylate ruthenium(II) dye (N719 dye, Solaronix) for 20 hours to load dye on the nanoporous TiO_2 electrode at room temperature. An acetonitrile-based electrolyte containing 50 mM tri-iodide (Solaronix SA, Iodolyte-AN50) was used for the electrolyte. (See Supplementary Information, Figure S7 for experimental procedures)

Field-emission scanning electron microscopy (FE-SEM, Hitachi S4800) was performed to observe the sample surface. The energy conversion performance of the DSSCs was evaluated using a solar simulator (Abet Technologies, model Sun 2000, 1000 W Xe source, Keithley 2400 source meter) under 1.5-AM 1-Sun conditions, calibrated by a KG-3 filter and NREL-certified reference cell without a mask. The electrochemical characterizations were performed using a BioLogic SP-300 potentiostat. The impedance spectra were acquired under open-circuit voltage, 1 Sun conditions.

Table 1 | Photovoltaic performance of textile-based dye-sensitized solar cells (DSSCs) prepared by sewing textile electrodes onto Hanji, cotton gauze, and silk gauze

Spacer	Voc (V)	Jsc (mA)	FF	η(%)
Paper	0.69	17.20	0.37	4.36
Cotton	0.67	15.59	0.47	5.00
Silk	0.69	19.70	0.43	5.83

1. O'Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature* **353**, 737–740 (1991).
2. Bach, U. *et al.* Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies. *Nature* **395**, 583–585 (1998).
3. Snaith, H. J. & Schmidt-Mende, L. Advances in liquid-electrolyte and solid-state dye-sensitized solar cells. *Adv Mater* **19**, 3187–3200 (2007).
4. Lenzmann, F. & Kroon, J. Recent advances in dye-sensitized solar cells. *Advances in OptoElectronics* **2007**, article ID 65073 , 1–10 (2007).
5. Ito, S. *et al.* High-efficiency (7.2%) flexible dye-sensitized solar cells with Ti-metal substrate for nanocrystalline-TiO_2 photoanode. *Chem. Comm.* 4004–4006 (2006).
6. Uchida, S., Tomiha, M., Takizawa, H. & Kawaraya, M. Flexible dye-sensitized solar cells by 28 GHz microwave irradiation. *J. Photochem. Photobiol. A.* **164**, 93–96 (2004).
7. Lindström, H. *et al.* A new method for manufacturing nanostructured electrodes on plastic substrates. *Nano Letters* **1**, 97–100 (2001).
8. Zhang, D., Yoshida, T., Oekermann, T., Furuta, K. & Minoura, H. Room-Temperature Synthesis of Porous Nanoparticulate TiO_2 Films for Flexible Dye-Sensitized Solar Cells. *Adv. Funct. Mater.* **16**, 1228–1234 (2006).
9. Cha, S. I. *et al.* Dye-sensitized solar cells on glass paper: TCO-free highly bendable dye-sensitized solar cells inspired by the traditional Korean door structure. *Energy Environ. Sci.* **5**, 6071–6075 (2012).

10. Fu, Y. *et al.* TCO-Free, Flexible, and Bifacial Dye-Sensitized Solar Cell Based on Low-Cost Metal Wires. *Adv. Energy Mater.* **2**, 37–41 (2012).
11. Fan, X. *et al.* Conductive mesh based flexible dye-sensitized solar cells. *Appl. Phys. Lett.* **90**, 073501-1–073501-3 (2007).
12. Dai, H. *et al.* Porous ZnO nanosheet arrays constructed on weaved metal wire for flexible dye-sensitized solar cells. *Nanoscale* **5**, 5102–5108 (2013).
13. Vijayakumar, V., Du Pasquier, A. & Birnie III, D. P. Electrical and optical studies of flexible stainless steel mesh electrodes for dye sensitized solar cells. *Solar Energy Mater. Solar Cells* **95**, 2120–2125 (2011).
14. Wang, H. *et al.* Low resistance dye-sensitized solar cells based on all-titanium substrates using wires and sheets. *Appl. Surf. Sci.* **255**, 9020–9025 (2009).
15. Zhang, L. *et al.* Fiber and fabric solar cells by directly weaving carbon nanotube yarns with CdSe nanowire-based electrodes. *Nanoscale* **4**, 4954–4959 (2012).
16. Fan, X. *et al.* Wire-Shaped Flexible Dye-sensitized Solar Cells. *Adv Mater* **20**, 592–595 (2008).
17. Cherenack, K., Zysset, C., Kinkeldei, T., Münzenrieder, N. & Tröster, G. Woven electronic fibers with sensing and display functions for smart textiles. *Adv Mater* **22**, 5178–5182 (2010).
18. Chen, T. *et al.* Intertwined aligned carbon nanotube fiber based dye-sensitized solar cells. *Nano letters* **12**, 2568–2572 (2012).
19. Huang, S. *et al.* Fibrous CdS/CdSe quantum dot co-sensitized solar cells based on ordered TiO_2 nanotube arrays. *Nanotechnology* **21**, 375201 (2010).
20. Lv, Z. *et al.* Highly efficient and completely flexible fiber-shaped dye-sensitized solar cell based on TiO_2 nanotube array. *Nanoscale* **4**, 1248–1253 (2012).
21. Yang, Z. *et al.* Photovoltaic Wire Derived from a Graphene Composite Fiber Achieving an 8.45 % Energy Conversion Efficiency. *Angew. Chem. Int. Ed.* **52**, 7545–7548 (2013).
22. Sun, H. *et al.* Quasi-solid-state, coaxial, fiber-shaped dye-sensitized solar cells. *J. Mater. Chem. A.* **2**, 345–349 (2014).
23. Pan, S. *et al.* Efficient dye-sensitized photovoltaic wires based on an organic redox electrolyte. *J. Am. Chem. Soc.* **135**, 10622–10625 (2013).
24. Chen, T. *et al.* Designing aligned inorganic nanotubes at the electrode interface: Towards highly efficient photovoltaic wires. *Adv. Mater.* **24**, 4623–4628 (2012).
25. Fu, Y. *et al.* Conjunction of fiber solar cells with groovy micro-reflectors as highly efficient energy harvesters. *Energy Environ. Sci.* **4**, 3379–3383 (2011).
26. Peng, M. *et al.* Integration of fiber dye-sensitized solar cells with luminescent solar concentrators for high power output. *J. Mater. Chem. A.* **2**, 926–932 (2014).

Acknowledgments

This work was supported by the "New & Renewable Energy Core Technology Program" of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Trade, Industry & Energy, Republic of Korea (No. 2011T100100678).

Author contributions

M. J. Y. and S. I. C. performed the textile based DSSC fabrication and wrote the manuscript. S. H. S. and D. Y. L. contributed in Fig. 2 and Fig. 4 by characterization and feedback to the fabrication process during study. All authors have reviewed the manuscript and agreed to submission.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Yun, M.J., Cha, S.I., Seo, S.H. & Lee, D.Y. Highly Flexible Dye-sensitized Solar Cells Produced by Sewing Textile Electrodes on Cloth. *Sci. Rep.* **4**, 5322; DOI:10.1038/srep05322 (2014).