



Wearable Solar Cells by Stacking Textile Electrodes**

Shaowu Pan, Zhibin Yang, Peining Chen, Jue Deng, Houpu Li, and Huisheng Peng*

Abstract: A new and general method to produce flexible, wearable dye-sensitized solar cell (DSC) textiles by the stacking of two textile electrodes has been developed. A metal-textile electrode that was made from micrometer-sized metal wires was used as a working electrode, while the textile counter electrode was woven from highly aligned carbon nanotube fibers with high mechanical strengths and electrical conductivities. The resulting DSC textile exhibited a high energy conversion efficiency that was well maintained under bending. Compared with the woven DSC textiles that are based on wire-shaped devices, this stacked DSC textile unexpectedly exhibited a unique deformation from a rectangle to a parallelogram, which is highly desired in portable electronics. This lightweight and wearable stacked DSC textile is superior to conventional planar DSCs because the energy conversion efficiency of the stacked DSC textile was independent of the angle of incident light.

Lightweight, portable electronic devices represent a mainstream direction in modern electronics.^[1–5] To this end, a lot of efforts have been directed towards the development of suitable energy sources to power these devices.^[6–10] In contrast to the more conventional planar solar cells, wire-shaped solar cells^[11–16] could be woven into flexible clothes by the well-developed textile technology. Both wire-shaped dye-sensitized and polymer solar cells have typically been made by twisting together two electrically conducting fibers as electrodes with photoactive materials between them.^[17,18] However, because of the difficulties in producing long effective fiber electrodes, the above wire-shaped cells have generally been limited to lengths of millimeters, and the energy conversion efficiencies largely decreased with an increase in cell length. Furthermore, it has been difficult to connect a number of

crossed, wire-shaped solar cells that had been woven into electronic textiles. Therefore, it remains challenging to weave such wire-shaped solar cells into efficient electronic textiles for practical applications.

Herein, a new and general method has been developed to produce flexible, wearable solar-cell textiles that are based on textile electrodes. Dye-sensitized solar cell (DSC) textiles with high efficiencies have been studied. A metal textile electrode that was made from micrometer-sized metal wires was used as the working electrode, whereas the textile counter electrode was woven from highly aligned carbon nanotube (CNT) fibers with high mechanical strengths and electrical conductivities. The two textile electrodes were stacked to obtain the desired DSC textile, which could be easily integrated into various fabrics or other flexible structures.

Modified titanium textiles were used as the working electrodes. To obtain the desired electrode materials, titanium wires with a diameter of 130 μm were woven into textiles. Aligned TiO_2 nanotubes were then perpendicularly grown on the titanium wire surface by electrochemical anodizing. Figure 1a shows a typical scanning electron microscopy (SEM) image of an anodized Ti wire textile. Aligned TiO_2 nanotubes with a diameter of 70–100 nm were produced on the surfaces of the Ti wires in the textile (Figure 1b and c). The lengths of the TiO_2 nanotubes can be controlled by varying the anodizing time to obtain nanotubes with lengths of 10, 18, 30, and 37 μm after 2, 4, 6, and 8 hours, respectively. After absorption of the dye N719, the Ti wire textile was used as the working electrode.

To prepare the CNT fiber textile, spinnable CNT arrays with a height of approximately 280 μm were first synthesized by chemical vapor deposition.^[19,20] The CNTs showed a multi-walled structure with an average diameter of 10 nm (Supporting Information, Figure S1). Aligned CNT sheets (with a thickness of ca. 20 nm) were continually pulled out of the array and then stacked into layered CNT films (thickness ca. 220 nm). The layered CNT films were further twisted into a CNT fiber with a uniform diameter of approximately 65 μm at a rotation speed of 2000 rpm (Figure S2 and S3). Finally, the CNT fibers were woven into textile electrodes with an average distance of approximately 600 μm between two neighboring parallel CNT fibers (Figure 1d and e). The resulting CNT fiber textile was flexible and could be bent into various shapes without breaking. A CNT fiber textile that has been closely attached onto a glass rod is shown in Figure 1f. No structure damage was detected by SEM after deformation of the CNT fiber textile.

The DSC textile was fabricated by stacking the CNT fiber textile onto the modified Ti textile, followed by incorporation of electrolyte (Figure 2). When a liquid electrolyte is used, the DSC textile needs to be sealed. The generation of photocurrent is illustrated in Figure S4. After absorption of the

[*] S. Pan, Z. Yang, P. Chen, J. Deng, H. Li, Prof. H. Peng
State Key Laboratory of Molecular Engineering of Polymers
Department of Macromolecular Science and Laboratory of
Advanced Materials, Fudan University
Shanghai 200438 (China)
E-mail: penghs@fudan.edu.cn

S. Pan, Prof. H. Peng
School of Materials Science and Engineering and Institute for
Advanced Materials and Nano Biomedicine
Tongji University
4800 Caoan Road, Shanghai 201804 (China)

[**] This work was supported by MOST (2011CB932503), NSFC (21225417), STCSM (12nm0503200), the Fok Ying Tong Education Foundation, the Program for Special Appointments of Professors at Shanghai Institutions of Higher Learning, and the Program for Outstanding Young Scholars from the Organization Department of the CPC Central Committee.



Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201402561>.

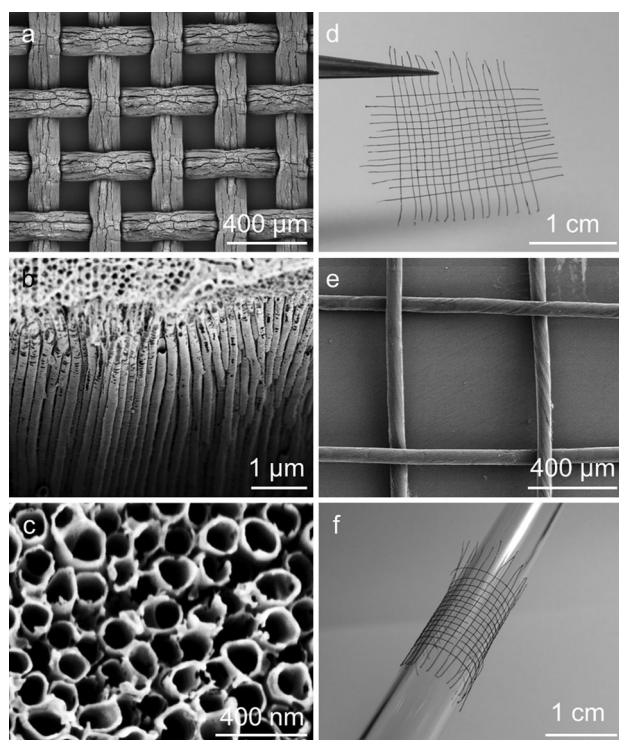


Figure 1. a) SEM image of the Ti wire textile modified with TiO_2 nanotubes. b, c) SEM images of TiO_2 nanotubes at low (b) and high magnification (c). d, e) Photograph (d) and SEM image (e) of a CNT fiber textile. f) Photograph of a CNT fiber textile wrapped around a glass rod.

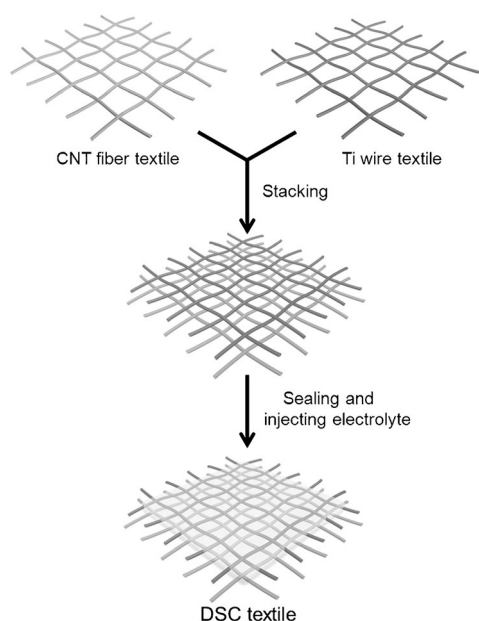


Figure 2. Fabrication of the DSC textile.

incident light, the excited dye molecule injects electrons into the conduction band of titanium dioxide. The electrons can be rapidly transported along the titanium-wire-based textile and reach the CNT fiber textile through the external circuit. Dye cations are reduced to the ground state by oxidation of I^- to

I_3^- ions, while the I_3^- ions are reduced to I^- ions by accepting electrons at the CNT fiber. The photocurrents are continuously produced by regeneration of the dye molecules and redox couples under illumination. Electrochemical impedance spectroscopy was used to investigate the DSC textile (Figure S5). The first semicircle that reflected the electrochemical reaction at the counter electrode in the high-frequency region was small in size, indicating a low electrical resistance with high catalytic activity for the CNT fiber textile electrode.

Furthermore, a series of DSC textiles that are based on different lengths of aligned TiO_2 nanotubes were fabricated, and their current density–voltage (J – V) curves are compared for four representative lengths in Figure 3a. The dependence of the photovoltaic parameters, including short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF), and energy conversion efficiency (η), on the length of the TiO_2 nanotube is shown in Figure 3a (see also Figures S6–S8). Similar to the calculation for the planar device, the effective

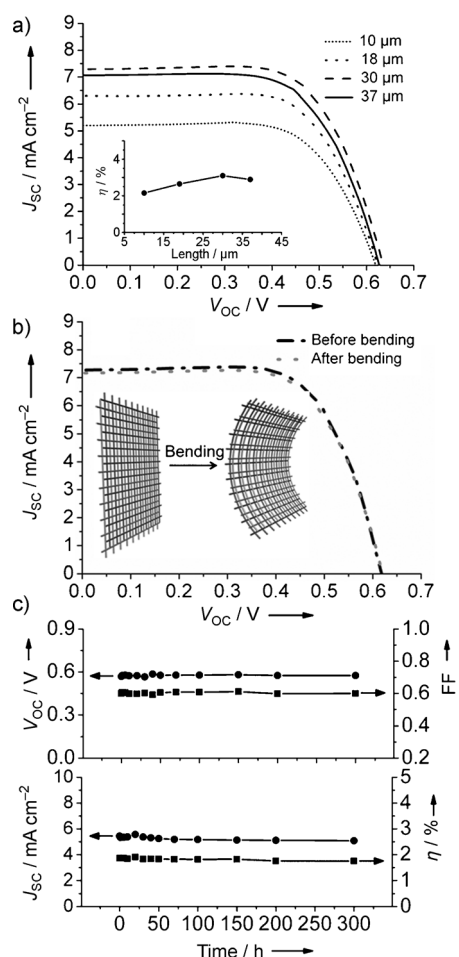


Figure 3. a) J – V curves of the DSC textile with an increase in the length of the TiO_2 nanotubes from 10 to 37 μm . Inset: Dependence of the energy conversion efficiency (η) on the length of the TiO_2 nanotubes. b) J – V curves of the DSC textile with a TiO_2 nanotube length of 30 μm before and after bending based on the liquid electrolyte. c) Time dependence of the photovoltaic parameters of the DSC textile that is based on the solid electrolyte.

area for calculating the energy conversion efficiency was obtained by multiplying length and width of the DSC textile (Figure S9). Both the V_{OC} and FF values remained almost unchanged with an increase in the length of the TiO_2 nanotubes, whereas the J_{SC} value first increased from 5.20 to 7.28 $mA\ cm^{-2}$ with an increase in length from 10 to 30 μm and then decreased to 7.06 $mA\ cm^{-2}$ when the length was further increased to 37 μm . With increasing length of the TiO_2 nanotubes, more dye molecules can absorb the incident light, which enhances the energy conversion efficiency. However, longer TiO_2 nanotubes also induce an increase in the electron transport pathway, which leads to more undesirable charge recombination reactions with lower efficiencies.^[21,22] As a result, the maximal energy conversion efficiency of 3.10% occurred at a length of 30 μm .

For the DSC textile with a grid structure, the dye molecules cannot only effectively absorb the incident sunlight from the working electrode of the modified Ti textile, but also from the counter electrode of the CNT fiber textile. Their $J-V$ curves for illumination from the two opposite directions are shown in Figure S10. Both V_{OC} and FF values were very similar, whereas the J_{SC} value for the illumination from the working electrode was appropriately 10% higher than for illumination from the counter electrode. In contrast, for the conventional planar DSC, the J_{SC} value for illumination from the counter electrode was just half of that for illumination from the working electrode (Figure S11). Furthermore, the conventional planar DSC showed decreasing energy conversion efficiencies when it was inclined with increasing angles from 0° to 60° for a fixed incident light beam. In contrast, because of its grid structure, the energy conversion efficiency of the DSC textile varied by less than 10% under the same conditions (Figure 4).

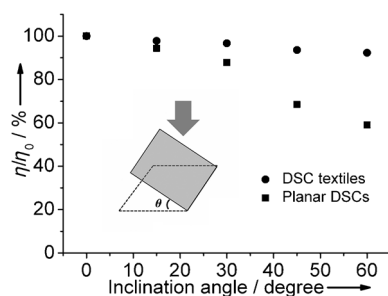


Figure 4. Dependence of the energy conversion efficiency on the incident light, measured by lifting one edge of a DSC textile with an angle of θ . Here, η_0 and η correspond to the energy conversion efficiencies at 0° and at an angle of θ , respectively.

Similar to the woven DSC textile that is derived from wire-shaped DSCs, the stacked DSC textile was also flexible. Figure 3b compares the $J-V$ curves of a DSC textile before and after bending, and these curves almost overlap. The energy conversion efficiencies of the DSC textile were further investigated with an increasing number of bending cycles (Figure S12). The energy conversion efficiencies varied by less than 10% over 100 cycles. To meet the practical requirements for flexible and portable electronic devices, the DSC

textile was further fabricated from the solid-state electrolyte with a highest energy conversion efficiency of approximately 2.1%, and the energy conversion efficiencies varied by less than 5% after 100 bending cycles (Figure S13 and S14). These DSC textiles were also stable with time when in use. The three photovoltaic parameters, V_{OC} , J_{SC} , and FF, were traced for a period of 300 hours in air (Figure 3c), and the energy conversion efficiencies decreased by less than 6%.

For the previously mentioned DSC textiles that were woven from the wire-shaped DSCs, the liquid electrolyte was typically located at the interface between CNT and TiO_2 , so that low energy conversion efficiencies were observed, for example, 0.12% (Figure S15). In contrast, when the electrodes were completely immersed in liquid electrolyte, charge transport to the entire length of the CNT fibers was improved, which led to much higher energy conversion efficiencies. Unlike the woven DSC textile, the stacked DSC textiles also exhibited a unique deformation aside from the bendable deformation that is based on flexibility. They could be reversibly deformed in a form similar to the widely used shutter (Figure 5). Because of a decrease in the effective

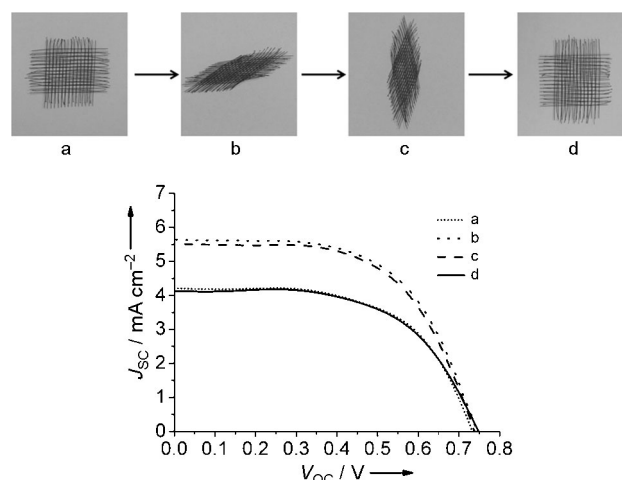


Figure 5. $J-V$ curves of a stacked DSC textile (Ti wire textile: 30 meshes) during a reversible deformation. The photographs a–d show the different shapes during one cycle of deformation.

illuminating area during the deformation (Figure S16), the energy conversion efficiencies could be further enhanced, for example by approximately 35% at a deformation angle of 45°. This unique deformation provides the stacked DSC textiles with properties that render them promising candidates for various portable electronic devices.

The energy conversion efficiency of the stacked DSC textile can be further increased by modifications of the structure. For instance, the incident light may penetrate the cavities, which leads to inefficient absorption that is due to the grid structure of the two textile electrodes. Figure 1a shows that the empty area amounts to approximately a quarter of the total textile area. The empty area may be filled with the additional electrode through the formation of a sandwich structure. To this end, a modified DSC textile with the CNT

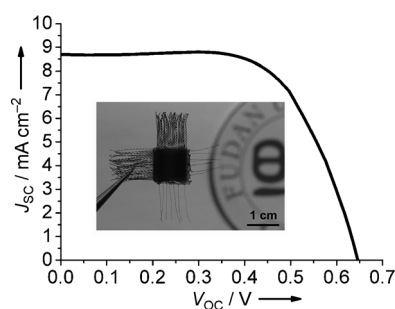


Figure 6. J - V curve of the DSC textile with the CNT fiber textile sandwiched between two Ti wire textiles. Inset: Photograph of a typical DSC textile with the sandwich structure.

fiber textile sandwiched by two Ti textiles was produced. Figure 6 shows a typical J - V curve of the modified DSC textile with a higher J_{sc} value of 8.69 mA cm^{-2} than for the previous non-sandwiched structure under the same conditions. As a result, the energy conversion efficiency increased to 3.62%, which corresponds to an enhancement of approximately 17%.

As expected, the DSC textile could be easily integrated into various flexible structures. Figure 7a and S17 show a DSC textile that had been woven into a fabric. Furthermore, the DSC textiles could be interconnected in series or in parallel to tune the output voltage or current. Figure S18 shows current-voltage (I - V) curves of two individual DSC textiles as well as of their connections in series and in parallel. The two DSC textiles displayed similar I - V curves. The textiles that were connected in series and in parallel displayed almost doubled outputs in terms of V_{oc} and I_{sc} , respectively.

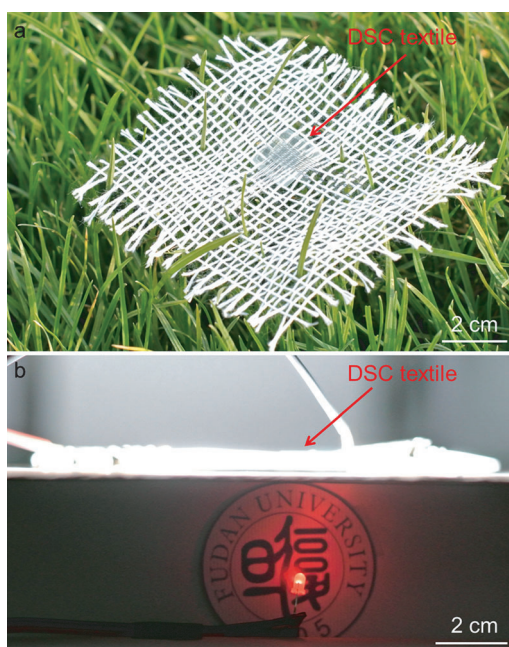


Figure 7. a) Photograph of a DSC textile integrated in a fabric. b) A red-light emission diode was lightened up by the DSC textile (five in series; for experimental details, see Video S1).

Based on this strategy, five DSC textiles were connected in series to efficiently power a red-light emission diode (Figure 7b and Video S1). DSCs were shown to be suitable for photovoltaic textiles mainly because of their high energy conversion efficiency according to previous studies on wire-shaped photovoltaic devices; the energy conversion efficiency was 4.6% for a wire-shaped DSC, but only 1.8% for a wire-shaped polymer solar cell with the same electrode.^[21,23] Furthermore, a solid-state electrolyte was used to replace the widely explored liquid electrolyte to produce stable DSC textiles.

In summary, we have developed a new and effective route to fabricate novel wearable DSC textiles that are based on textile electrodes. These DSC textiles exhibited high energy conversion efficiencies of up to 3.67%, which were well maintained during bending. They could also be easily connected to tune the output voltage. The use of these wearable DSC textiles to drive a light-emitting diode has been successfully demonstrated. This work also provides a general method for the development of wearable energy devices.

Experimental Section

Fabrication of Ti wire textile electrodes: Ti wires with a diameter of $130 \mu\text{m}$ were woven into textiles (80 meshes), which were then washed with acetone, isopropanol, and ethanol. Perpendicularly aligned TiO_2 nanotubes were grown on the Ti wires by electrochemical anodizing in an ethylene glycol solution that contained NH_4F (0.3 wt %) and deionized water (8 wt %) at a voltage of 60 V for 2, 4, 6, or 8 hours. The electrochemical anodizing was carried out in a two-electrode electrochemical cell with the Ti wire textile and the Pt sheet as anode and cathode, respectively. The modified Ti wire textile was washed with deionized water to remove the electrolyte, followed by annealing at 500°C in air for 1 hour. The annealed Ti wire textile was then immersed into an aqueous solution of TiCl_4 (100 mM) at 70°C for 30 min, followed by annealing at 450°C for 30 min. The material was immersed into a solution of N719 (0.3 mM) in a solvent mixture of *tert*-butanol and dry acetonitrile (1:1, v/v) for 16 hours while the temperature was cooled to 120°C .

Fabrication of DSC textiles: A typical DSC textile was fabricated by stacking of the Ti wire textile with incorporated N719 as the working electrode and the CNT fiber textile as the counter electrode, followed by coating of the redox electrolyte. For the liquid electrolyte, which was composed of lithium iodide (0.1M), iodine (0.05M), 1,2-dimethyl-3-propylimidazolium iodide (0.6M), and 4-*tert*-butyl-pyridine (0.5M) in dry acetonitrile, the textile was incorporated and sealed between two poly(ethylene terephthalate) membranes for the measurements. The two sealing membranes were pressed with a Surlyn frame at 120°C . The solid electrolyte was composed of 1-ethyl-3-methylimidazolium iodide (4.96 g), 1-propyl-3-methylimidazolium iodide (1.19 g), and iodine (0.05 g).

Received: February 19, 2014

Published online: April 30, 2014

Keywords: dye-sensitized solar cells · electron transfer · energy conversion · light-emitting diodes

[1] H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737–738.

[2] M. Koo, K. I. Park, S. H. Lee, M. Suh, D. Y. Jeon, J. W. Choi, K. Kang, K. J. Lee, *Nano Lett.* **2012**, *12*, 4810–4816.

- [3] M. Kaltenbrunner, M. S. White, E. D. Glowacki, T. Sekitani, T. Someya, N. S. Sariciftci, S. Bauer, *Nat. Commun.* **2012**, *3*, 770.
- [4] J. Ren, W. Bai, G. Guan, Y. Zhang, H. Peng, *Adv. Mater.* **2013**, *25*, 5965–5970.
- [5] Y. H. Lee, J. S. Kim, J. Noh, I. Lee, H. J. Kim, S. Choi, J. Seo, S. Jeon, T. S. Kim, J. Y. Lee, J. W. Choi, *Nano Lett.* **2013**, *13*, 5753–5761.
- [6] M. Armand, J. M. Tarascon, *Nature* **2008**, *451*, 652–657.
- [7] B. C. H. Steele, A. Heinzl, *Nature* **2001**, *414*, 345–352.
- [8] A. Hagfeldt, M. Gratzel, *Acc. Chem. Res.* **2000**, *33*, 269–277.
- [9] R. O'Hayre, D. Braithwaite, W. Hermann, S. J. Lee, T. Fabian, S. W. Cha, Y. Saito, F. B. Prinz, *J. Power Sources* **2003**, *124*, 459–472.
- [10] T. Chen, L. Qiu, Z. Yang, Z. Cai, J. Ren, H. Li, H. Lin, X. Sun, H. Peng, *Angew. Chem.* **2012**, *124*, 12143–12146; *Angew. Chem. Int. Ed.* **2012**, *51*, 11977–11980.
- [11] D. Zou, D. Wang, Z. Chu, Z. Lv, X. Fan, *Coord. Chem. Rev.* **2010**, *254*, 1169–1178.
- [12] T. Chen, L. Qiu, Z. Yang, H. Peng, *Chem. Soc. Rev.* **2013**, *42*, 5031–5041.
- [13] S. Pan, Z. Yang, H. Li, L. Qiu, H. Sun, H. Peng, *J. Am. Chem. Soc.* **2013**, *135*, 10622–10625.
- [14] D. Liu, M. Zhao, Y. Li, Z. Bian, L. Zhang, Y. Shang, X. Xia, S. Zhang, D. Yun, Z. Liu, A. Cao, C. Huang, *Acs Nano* **2012**, *6*, 11027–11034.
- [15] B. Weintraub, Y. Wei, Z. L. Wang, *Angew. Chem. Int. Ed.* **2009**, *48*, 8981–8985; *Angew. Chem.* **2009**, *121*, 9143–9147.
- [16] Z. Yang, H. Sun, T. Chen, L. Qiu, Y. Luo, H. Peng, *Angew. Chem. Int. Ed.* **2013**, *52*, 7545–7548; *Angew. Chem.* **2013**, *125*, 7693–7696.
- [17] X. Fan, Z. Chu, F. Wang, C. Zhang, L. Chen, Y. Tang, D. Zou, *Adv. Mater.* **2008**, *20*, 592–595.
- [18] T. Chen, L. Qiu, Z. Cai, F. Gong, Z. Yang, Z. Wang, H. Peng, *Nano Lett.* **2012**, *12*, 2568–2572.
- [19] W. Guo, C. Liu, F. Zhao, X. Sun, Z. Yang, T. Chen, X. Chen, L. Qiu, X. Hu, H. Peng, *Adv. Mater.* **2012**, *24*, 5379–5384.
- [20] X. Zhang, Q. Li, Y. Tu, Y. Li, J. Y. Coulter, L. Zheng, Y. Zhao, Q. Jia, D. E. Peterson, Y. Zhu, *Small* **2007**, *3*, 244–248.
- [21] T. Chen, L. Qiu, H. G. Kia, Z. Yang, H. Peng, *Adv. Mater.* **2012**, *24*, 4623–4628.
- [22] Z. Liu, V. Subramania, M. Misra, *J. Phys. Chem. C* **2009**, *113*, 14028–14033.
- [23] Z. Zhang, Z. Yang, Z. Wu, G. Guan, S. Pan, Y. Zhang, H. Li, J. Deng, B. Sun, H. Peng, *Adv. Energy Mater.* **2014**, DOI: 10.1002/aenm.201301750.