

Pen-Writing Polypyrrole Arrays on Paper for Versatile Cheap Sensors

Hanyu Jia,[†] Jian Wang,[†] Xinyue Zhang, and Yapei Wang*

Department of Chemistry, Renmin University of China, Beijing, 100872 China

S Supporting Information

ABSTRACT: A simple and low-cost “pen-writing” method is exploited for integrating conducting polymer on cellulosic paper. The pen-written paper chip not only possesses excellent mechanical and electrical properties, but also serves as a versatile sensor, fulfilling several real-time and in situ detections for ammonia gas, thermal heating, and NIR light. The theoretical detection limit of ammonia gas can be as low as 1.2 ppm, which is a promising performance for industrial application. In addition, this “pen-writing” technique can be extended to generate wearable electrical textiles in a large scale.

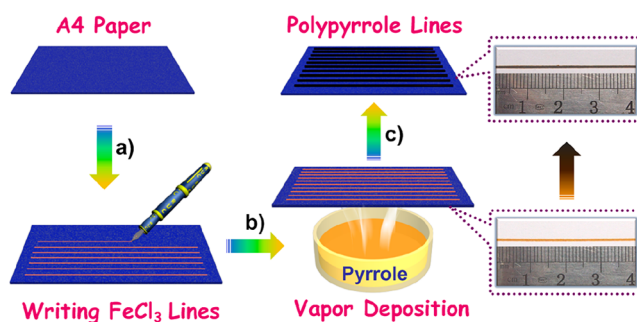


Great concerns over the increasing environmental pollution have urged better detection techniques for harmful agents.¹ Real time and in situ analysis of ambient information is the most critical demand for designing functional sensors.² Even though providing precise analysis, traditional laboratory instruments are expensive and heavy; paper-based sensors with respect to low cost and portability are meeting many public requirements and becoming more and more welcome.³

Growing efforts are devoted to exploiting electronic paper devices with both excellent sensing ability and outstanding technical practicability.⁴ Narrowing the deposition of active materials that are sensitive to environmental changes on paper can dramatically improve the sensitivity of detection.⁵ Techniques such as lithography and chemical vapor deposition can create sensing arrays with precise control over feature size, yet they are inconvenient and costly.⁶ Inkjet printing is popular nowadays in terms of its easy control by software on PC. This technique is undoubtedly amenable to fabricating desirable circuits on paper in a short process with low cost.⁷ However, elaborate preparation of ink formulation is on demand to ensure the printed features continuous enough and inject nozzles not to be blocked.

Despite compromised accuracy and precision, pen-writing has no critical requirement for the ink and is easily operated. Fresh paper chips can be rapidly fabricated without supporting equipments, affording great convenience for practical use in resource-limited areas. Examples of functional paper devices by pen-writing are still rare so far. Few conductive “inks” such as silver pulp,⁸ carbon nanotube solution,⁹ carbon nanotube pellet,¹⁰ and graphene¹¹ have been attempted. Among them, only the paper chip with carbon nanotube stripes was assessed for gas detection.¹⁰ Conducting polymers have been widely used as active materials in the preparation of various sensors. In this work, we successfully deposited polypyrrole on paper using oxidative inks through a low-cost and simple “pen-writing” method. The written paper chip serves as a portable multifunctional sensor for the detection of ammonia, temperature, and near-infrared light.

Pen-writing polypyrrole on A4 paper is illustrated in Scheme 1. The writing began with a pen filled with saturated FeCl_3

Scheme 1. Schematic Illustration of Pen-Writing Polypyrrole on A4 Paper^a

^a(a) Pen-writing FeCl_3 solution on the paper. (b) Exposing the FeCl_3 lines to pyrrole vapor. (c) Interfacial polymerization of pyrrole along the FeCl_3 lines. Insets are photographs of A4 paper written with FeCl_3 and polypyrrole after fumigation. The pen has an Iridium nib that is inert to FeCl_3 .

solution. First, typical straight lines of FeCl_3 were manually drawn on a piece of A4 paper. Then, the paper with FeCl_3 lines was exposed to pyrrole vapor, leading to quick interfacial polymerization of pyrrole on the paper. The mechanism of polymerization was ascribed to the oxidation of pyrrole by FeCl_3 , forming conjugative structures.¹² As shown in the inset photographs, the color of a written line changed from yellow to black after brief fumigation, indicating the polymerization is fast. Finally, water in the ink was fully dried to yield robust polypyrrole stripes on the paper. Nonstraight lines or complex

Received: October 11, 2013

Accepted: December 27, 2013

Published: December 31, 2013

features could also be constructed on paper by means of this pen-writing method.

Three factors, including polymerization time, polymerization temperature, and oxidant concentration, were evaluated to discern their impact on the conductivity of polypyrrole. The A4 paper is electrically insulated with a sheet resistance of over $10^{15} \Omega\text{sq}^{-1}$,^{4a} while it became highly conductive with the deposition of polypyrrole. As shown in Figure 1e, at a given temperature of

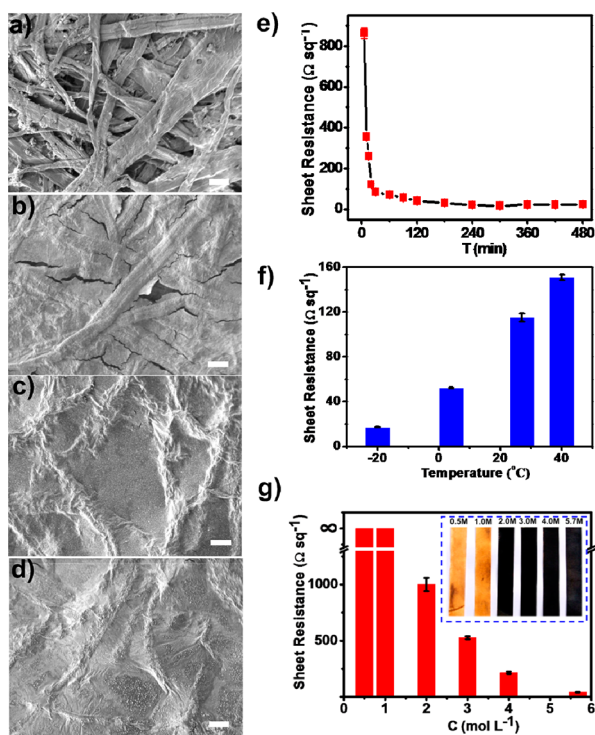


Figure 1. SEM images of A4 paper coated with polypyrrole at different polymerization time: (a) 0, (b) 5, (c) 90, and (d) 300 min. Scale bar: 10 μm . The sheet resistance of A4 papers coated with polypyrrole against different conditions: (e) The influence of polymerization time at a given temperature of $-20\text{ }^\circ\text{C}$; (f) The influence of polymerization temperature (the polymerization time was 90 min); (g) The influence of FeCl_3 concentration: 0.5, 1.0, 2.0, 3.0, 4.0, and 5.67 M (saturated). Polymerization was performed at $-20\text{ }^\circ\text{C}$ for 90 min. Inset photograph of (g) is the paper coated with polypyrrole at different FeCl_3 concentrations.

$-20\text{ }^\circ\text{C}$, the sheet resistance declined upon increasing the polymerization time. A plateau with a minimum sheet resistance of about $17 \Omega\text{sq}^{-1}$ was eventually reached after 90 min. Figure 1a–d summarized SEM images of the A4 paper deposited with polypyrrole at different polymerization time. The pristine paper possesses a distinct porous feature, while it was partially covered with a thin layer of polypyrrole (Figure 1b) at the beginning of polymerization. After polymerizing for 90 min, the fiber-crossing-like feature of the paper was almost lost. Instead, the coverage of polypyrrole film, in turn, became more compact and continuous. These SEM observations well elucidated that the conductance was enhanced with the increase of polymerization time.

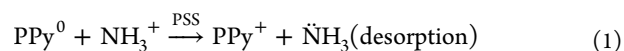
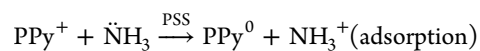
Decreasing polymerization temperature was able to improve the conductance of polypyrrole. As shown in Figure 1f, four polymerization temperatures were studied over the same time (90 min), including $-20\text{ }^\circ\text{C}$, which is close to the freezing point of pyrrole, $4\text{ }^\circ\text{C}$, which is slightly above the freezing point of

water, $27\text{ }^\circ\text{C}$, which is the room temperature, and $39\text{ }^\circ\text{C}$, which is the flashing point of pyrrole. A lowest sheet resistance of $17 \Omega\text{sq}^{-1}$ was acquired at $-20\text{ }^\circ\text{C}$. At this stage, the volatilization of pyrrole was extremely hindered, hence decelerating the rate of polymerization. It was hypothesized that unfavorable cross-linking or branching of the polymer was effectively avoided at lower temperature, leading to a longer conjugation length and a more ordered structure.¹³ As a result, the conductivity of polypyrrole was significantly enhanced.

FeCl_3 concentration also exhibited great effect on the conductance of polypyrrole. Increasing the oxidant concentration can shorten the polymerization process and simultaneously improve the conductivity of polypyrrole, as shown in Figure 1g. It is assumed that more oxidant could tailor the polymer to be more compact and continuous. However, there was no obvious polypyrrole generated on paper if the FeCl_3 concentration was below 1 M.

Pen-writing polypyrrole renders the possibility for the paper to serve as a flexible and foldable electronic device with conductive circuits. Room temperature was preferred for vapor polymerization in order to conveniently fabricate paper devices. There was no need for heating or cooling the synthetic system, hence translating into vast energy saving and reduction in equipment. To identify the influence of mechanical bending on the conductance, a paper chip with a polypyrrole stripe was prepared and subsequently deposited with two gold electrodes. The current output was recorded on an electrochemical workstation with an applied direct voltage. As shown in Figure 2a, the current change was negligible at several bending states. There was only a 1.6% increase of the current when the two gold electrodes were moved close to each other (1 cm). The little current change was attributed to the enhanced electrical contact among cellulose fibers at a bending status. The device maintained its integrity with an unchanged conductance after bending and straightening for 27 cycles (Figure 2b). SEM images (Figure 2e–g) revealed that polypyrrole not only continuously covered the paper surface, but also penetrated into the paper. It should be noted that more complicated circuits could be written in addition to straight lines. As shown in Figure 2c and d, two separated circuits were prepared by means of pen-writing. Each circuit has a resistance of unit length less than $1000 \Omega\text{cm}^{-1}$. A yellow LED mounted between two circuits was lit up at a low voltage. The ease of fabrication, with the combination of good conductance and stability, promises these paper chips for multifunctional detections, as discussed in detail below.

Paper chips consisting of polypyrrole arrays are at the forefront of devising multifunctional sensors, owing to the unique activity of polypyrrole to various environments.¹⁴ A typical paper chip with a polypyrrole stripe (Figure 3a, inset) was anchored on a power supply through two gold electrodes. The electrical readout keeps unchanged until the polypyrrole meets an environmental change. With respect to the charge-transfer interaction,¹⁵ the adsorption of ammonia can effectively reduce the number of mobile carriers in the polymer, thus, impairing the conductance of polypyrrole (eq 1).



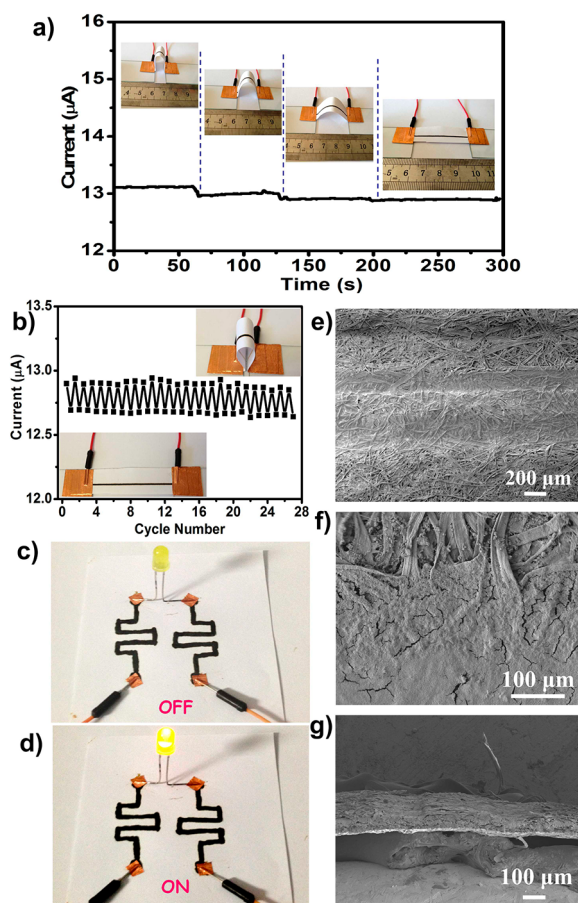


Figure 2. (a) Current–time curve of a paper device with an applied voltage of 1.0 V at different bending states. The effective length is 4 cm. (b) Current–bending cycles of the paper chip at a given voltage. Optical photographs of a yellow LED mounted between two polypyrrole circuits with an applied voltage of (c) 0 and (d) 3.0 V. (e, f) Top view and (g) sectional view of polypyrrole on an A4 paper.

To quantify the sensing ability, the signal output was normalized by the absolute change of conductivity $-\Delta G/G_0$ (%) as in eq 2:

$$-\Delta G/G_0(\%) = [(I_0 - I)/I_0] \times 100 \quad (2)$$

where G_0 and I_0 are the initial conductivity and current before the sensing test, and I is the current after exposure to ammonia with a specific concentration. As shown in Figure 3a, the change of conductivity reached 3.08% upon exposure to ammonia with a concentration of 100 ppm. However, the output current signal turned too weak to be readily recorded when the ammonia concentration became lower. This limitation is a common drawback for polypyrrole because of its poor interaction with ammonia gas. To improve the sensitivity of paper chips, poly(sodium-*p*-styrenesulfonate) (PSS), as a polyacid that can bind with Lewis base, was codissolved in the initial ink to dope the polypyrrole arrays. IR spectroscopy confirmed the successful loading of PSS into the conducting polymer. As shown in Figure S1, new bands at 1195 and 1036 cm^{-1} relative to pure polypyrrole are ascribed to the asymmetric and symmetric stretching vibration of sulfonic acid group, respectively. Remarkably, the change of conductivity in the presence of 100 ppm ammonia was improved to 6.25% with 1.0 wt % PSS. Since the addition of PSS did not affect the conductivity of the resulting paper chips, the

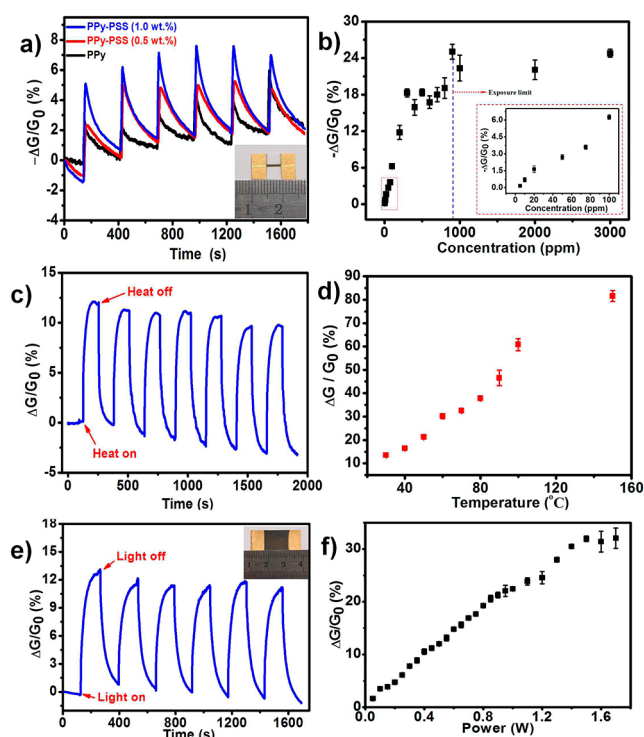


Figure 3. (a) Ammonia (100 ppm) response of paper chips doped with or without PSS. The applied voltage is 1.0 V. Inset is the photograph of a typical paper chip. (b) Gas-sensing tests of paper chips doped with 1.0 wt % PSS in the presence of ammonia with concentration ranging from 5–3000 ppm. Inset: the first six points in the graph. (c) On–off cycles of the thermal response of a paper chip between 30 °C and room temperature. (d) The response of the paper chip to different temperatures. (e) On–off cycles of NIR (808 nm) response of a paper chip. Inset is the photograph of a typical paper chip for light-sensing tests. NIR power is 0.5 W. (f) NIR sensing tests with the light power ranging from 0.05–1.70 W.

improvement of sensitivity should be attributed to the enhanced interaction between the polymer blend and ammonia gas. For the paper chip doped with 1.0 wt % PSS, conductivity change was still detectable even when ammonia concentration was as low as 5 ppm. The theoretical detection limit (DL) was estimated by analyzing a sensing curve at 5 ppm ammonia, with 100 consecutive points randomly selected to calculate the standard deviation. DL varies with the standard deviation (SD) of blank values and the average peak height (APH), $DL = 3SD \times 5/APH$. A detection limit of 1.2 ppm was obtained from the calculation result. Excessive exposure did not cause the sensing chip to output stronger signals when the ammonia concentration was over 900 ppm (Figure 3b). However, this exposure limit is already 30 times above the point at which ammonia can be freely smelt by human nose.

Besides responding to ammonia gas, the paper chip is intrinsically sensitive to thermal treatment. To identify its thermal sensitivity, a paper chip having a straight polypyrrole stripe was exposed to a given temperature for 100 s to ensure thermal equilibrium. As shown in Figure 3c, the conductivity change ($\Delta G/G_0$) abruptly jumped 13.42% when the paper chip was transferred from room temperature (25 °C) to 30 °C. The new conductivity was retained at a high level until the environment returned to room temperature. Contrary to ammonia gas, thermal heating routinely strengthens the conductivity of polypyrrole. As a p-type semiconductor,

polypyrrole transfers charges based on electron-deficient holes. Ammonia as an electron-donor can neutralize free holes thus leading to the increase of resistance. However, thermal excitation, on the contrary, rapidly increases the number and mobility of effective carriers, resulting in the decrease of resistance.¹⁶ The change of conductivity was positively correlated with the temperature. As shown in Figure 3d, the conductivity change reached up to $81.55\% \pm 2.34\%$ at $150\text{ }^\circ\text{C}$. It should be noted that the paper chip was limited to much higher temperature because the enameled wires were involved in the integrated circuit. The thermally sensitive nature of the paper chip is appropriate for biological application. As a proof of concept, the paper chip was utilized to test human's mouth and palm temperature. Subtle differences among three persons could be roughly distinguished (Figure S2).

Polypyrrole is able to convert near-infrared light (NIR) to thermal heat.¹⁷ As such, NIR irradiation (808 nm) can trigger electrical response of the conducting polymer on the basis of thermal excitation effect. To adequately collect lights from the laser source, a typical paper chip ($1 \times 1\text{ cm}^2$ square) fully painted with an active layer of polypyrrole was exploited for NIR detection. Analogue to thermal response, the conductivity of the paper chip was increased immediately upon exposure to NIR. A reproducible on–off response with a significant conductivity change (12.0%) was achieved by laying the paper chip between in NIR light (0.5 W) and in dark (Figure 3e). The conductivity change was almost proportionally relevant to the dose of NIR irradiation, which yet stopped at 32.0% when the power reached over 1.5 W, because the severe irradiation tended to burn the paper chip (Figure 3f). It should be noted that the paper chip has no electrical response to UV light or visible light, ensuring that the NIR detection can not be interfered by ambient light.

To readily extend our writing technology for more potential, conducting polypyrrole was installed into textiles via an amended “pen-writing” approach. As shown in Figure 4a, cotton threads composed of cellulose fibers ($\sim 20\text{ }\mu\text{m}$ in diameter, Figure 4c) were loosely wound on a metallic frame. Instead of regular pens, a brush pen was employed to paint the cotton threads FeCl_3 ink. Subsequent polymerization in the presence of pyrrole vapor led to the formation of polypyrrole on cotton threads (Figure 4b). SEM investigation revealed that polypyrrole had successfully grown from the surface to the interior of cotton threads, indicating a deep polymerization running through the whole matrix (Figure 4d,e). The resulting threads were flexible and mechanically stable which could be wound around a centrifugal tube for dozens of rounds without damage, as illustrated in Figure 4f. Importantly, the growth of polypyrrole endowed cotton threads with intriguing electrical performance. The cotton thread had an average resistance of unit length less than $500\text{ }\Omega\text{ cm}^{-1}$ and could readily act as electrical wires to light up a LED lamp under an applied voltage. Moreover, the application of these conducting threads could be readily weaved into textiles. As shown in Figure 4h,i, our university logo, RUC, was manually weaved on a piece of cloth using the as-synthesized conducting threads. The logo acted as a fantastic circuit, being conductive enough to light up the LED lamp at a low voltage.

In summary, we demonstrated a simple, low-cost and conventional “pen-writing” method for integrating polypyrrole into cheap paper-based matrix. The paper chip served as a versatile real-time sensor, fulfilling several sensing tests for ammonia gas, thermal heat, and NIR irradiation. Optimally

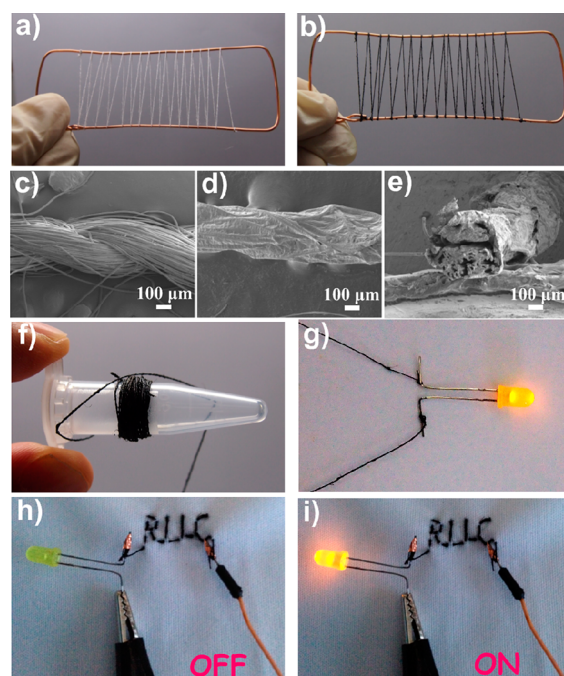


Figure 4. Photographs of (a) neat cotton threads, and (b) cotton threads grown with polypyrrole on a copper frame. SEM images of (c) neat cotton wire, (d) top view, and (e) sectional view of cotton threads grown with polypyrrole. (f) Conducting cotton threads wound around a centrifugal tube. (g) A yellow LED was lighted up under 4.0 V using conducting cotton threads as electrical connecting wires. A piece of cloth weaved with a RUC logo by the conducting cotton threads as a circuit to light a yellow LED (h) off and (i) on.

formulating the ink upon addition of additives can intensively improve the sensing performance, e.g. the paper chip loaded with polyacid exhibited enhanced sensitivity to ammonia gas. Capable of feeling body temperature and NIR irradiation so sensitively, the paper chip seems translational as a thermometer or photometer in biological systems. We believe that this “pen-writing” technique offers a generally applicable approach for rapidly fabricating fresh paper sensors without expensive instruments, providing great convenience for practical application in resource-limited areas. In addition to sensor fabrication, the writing technique was extended onto textiles, such as converting insulative cotton threads to electrically conductive wires. Intending for practical detection without complicated synthesis, our current work only focused on the fabrication at room temperature. However, adjusting the polymerization temperature is envisioned to afford materials with better conductance and flexibility, being great candidates as electrodes for wearable electronics on human clothes.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental section and data section, which includes the FTIR spectra and supplementary sensing test for human temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yapei.wang@ruc.edu.cn.

Author Contributions

†These authors contributed equally to this work (H.J. and J.W.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (51373197) and Trans-Century Training Programme Foundation for the Talents by the State Education Commission (NCET-12-0530).

REFERENCES

- (1) (a) Potyrailo, R. A.; Surman, C.; Nagraj, N.; Burns, A. *Chem. Rev.* **2011**, *111*, 7315–7354. (b) Rceck, F.; Barsan, N.; Weimar, U. *Chem. Rev.* **2008**, *108*, 705–725. (c) Stizel, S. E.; Aernecke, M. J.; Walt, D. R. *Annu. Rev. Biomed. Eng.* **2011**, *13*, 1–25.
- (2) (a) Wilson, A. D.; Baietto, M. *Sensors* **2009**, *9*, 5099–5148. (b) Zou, X.; Wang, J.; Liu, X.; Wang, C.; Jiang, Y.; Wang, Y.; Xiao, X.; Ho, J. C.; Li, J.; Jiang, C.; Fang, Y.; Liu, W.; Liao, L. *Nano Lett.* **2013**, *13*, 3287–3292. (c) Kauffmann, D. R.; Star, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6550–6570. (d) Novotney, J. L.; Dichtel, W. R. *ACS Macro Lett.* **2013**, *2*, 423–426.
- (3) (a) Maxwell, E. J.; Mazzeo, A. D.; Whitesides, G. M. *MRS Bull.* **2013**, *38*, 309–314. (b) Lewis, G. G.; DiTucci, M. J.; Phillips, S. T. *Angew. Chem., Int. Ed.* **2012**, *51*, 12707–12710.
- (4) (a) Tobjörk, D.; Österbacka, R. *Adv. Mater.* **2011**, *23*, 1935–1961. (b) Hu, L.; Cui, Y. *Energy Environ. Sci.* **2012**, *5*, 6423–6435. (c) Lee, H. M.; Choi, S.-Y.; Jung, A.; Ko, S. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 7718–7723. (d) Mazzeo, A. D.; Kalb, W. B.; Chan, L.; Killian, M. G.; Bloch, J.-F.; Mazzeo, B. A.; Whitesides, G. M. *Adv. Mater.* **2012**, *24*, 2850–2856. (e) Yuan, L.; Yao, B.; Hu, B.; Huo, K.; Chen, W.; Zhou, J. *Energy Environ. Sci.* **2013**, *6*, 470–476.
- (5) Wang, J.; Zhang, X.; Huang, X.; Wang, S.; Qian, Q.; Du, W.; Wang, Y. *Small* **2013**, *9*, 3759–3764.
- (6) Martinez, A. W.; Phillips, S. T.; Whitesides, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 19606–19611.
- (7) (a) Jang, J.; Ha, J.; Cho, J. *Adv. Mater.* **2007**, *19*, 1772–1775. (b) Yoon, B.; Ham, D.-Y.; Yarimaga, O.; An, H.; Lee, C. W.; Kim, J.-M. *Adv. Mater.* **2011**, *23*, 5492–5497.
- (8) Russo, A.; Ahn, B. Y.; Adams, J. J.; Duoss, E. B.; Bernhard, J. T.; Lewis, J. A. *Adv. Mater.* **2011**, *23*, 3426–3430.
- (9) Hu, L.; Choi, J. W.; Yang, Y.; Jeong, S.; Mantia, F. L.; Cui, L.; Cui, Y. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 21490–21494.
- (10) Mirica, K. A.; Weis, J. G.; Schnorr, J. M.; Esser, B.; Swager, T. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 10740–10745.
- (11) Hyun, W. J.; Park, O. O.; Chin, B. D. *Adv. Mater.* **2013**, *25*, 4729–4734.
- (12) Machida, S.; Miyata, S.; Techagumpuch, A. *Synth. Met.* **1989**, *31*, 311.
- (13) Qi, G.; Huang, L.; Wang, H. *Chem. Commun.* **2012**, *48*, 8246–8248.
- (14) (a) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19–24. (b) Bai, H.; Shi, G. *Sensors* **2007**, *7*, 267–307. (c) An, K. H.; Jeong, S. Y.; Hwang, H. R.; Lee, Y. H. *Adv. Mater.* **2004**, *16*, 1005–1009. (d) Hamilton, S.; Hephher, M. J.; Sommerville, J. *Sens. Actuators, B* **2005**, *107*, 424–432. (e) Dong, B.; Krutschke, M.; Zhang, X.; Chi, L.; Fuchs, H. *Small* **2005**, *1*, 520–524.
- (15) (a) Bhat, N. V.; Gadre, A. P.; Bambole, V. A. *J. Appl. Polym. Sci.* **2001**, *80*, 2511–2517. (b) Yoon, H.; Chang, M.; Jang, J. *J. Phys. Chem. B* **2006**, *110*, 14074–14077. (c) Virji, S.; Huang, J.; Kaner, R. B.; Weiller, B. H. *Nano Lett.* **2004**, *4*, 491–496. (d) Bradley, K.; Gabriel, J. P.; Briman, M.; Star, A.; Grüner, G. *Phys. Rev. Lett.* **2003**, *91*, 218301.
- (16) Heeger, A. J.; Sariciftci, N. S.; Nanddas, E. B. *Semiconducting and Metallic Polymer*; Oxford University Press: New York, 2010.
- (17) Yang, K.; Xu, H.; Cheng, L.; Sun, C.; Wang, J.; Liu, Z. *Adv. Mater.* **2012**, *24*, 5586–5592.