7730 *J. Am. Chem. Soc.* **2001,** *123,* 7730−7731

A Conducting Polymer Nanojunction Switch

Huixin He,[†] Jisheng Zhu,[†] Nongjian J. Tao,[*,†]
Larry A. Nagahara,[‡] Islamshah Amlani,[‡] and Raymond Tsui[‡]

Department of Physics, Florida International University
Miami, Florida 33199
Physical Sciences Research Laboratories, Motorola Labs
7700 South River Parkway, Tempe, Arizona 85284

Received May 24, 2001
Revised Manuscript Received June 25, 2001

The recent surge of interest in nanomaterials is driven by not only the need of ever-increasing miniaturization of microelectronics but also the discovery of many novel phenomena that occur on the nanoscale.[1] Conducting polymers are attractive for a variety of applications.[2] Bulk polymer materials are often described as highly conductive nanocrystalline domains separated with less conductive disordered regions.[3] The inhomogeneity has been a serious hindrance for a complete understanding of the materials as well as for many applications. To date, most works have focused on bulk samples, which measure properties averaged out over many nanocrystalline domains and disordered regions. Because nanocystalline domains are as small as a few nanometers, directly probing each individual domains is not a trivial task. In this communication, we report a study of charge transport through a polyaniline nanojunction formed between two nanoelectrodes separated with a gap comparable to the size of a nanocrystalline domain. In sharp contrast to bulk samples whose conductance varies smoothly between insulating and conducting states as a function of the electrochemical potential, the polymer nanojunction switches *abruptly* between the two states, in the fashion of a digital switch. The nanojunction can switch much faster with less power than larger junctions, and may be exploited in sensor applications.

Wrighton et al.[4] have pioneered a conducting polymer microelectrochemical transistor to measure the electrical properties of polymer materials between two microfabricated electrodes by controlling the electrochemical potential of the electrodes. A crucial task of our experiment is to fabricate a pair of nanoelectrodes with a gap of a few nanometers or less, which is achieved using two methods. The first method[5] starts with a pair of Au nanoelectrodes with a 20−80 nm gap on an oxidized Si substrate by electron beam lithography. We then further reduce the gap by electrochemically depositing Au onto the nanoelectrodes, using the tunneling current between the nanoelectrodes as feedback. The closest distance between the nanoelectrodes is ~1 nm, estimated from the tunneling current, and the radius of curvature of each nanoelectrode is between 5 and 15 nm (Figure 1). The second method uses a STM setup,[6] which can produce similar results but is more susceptible to drift.

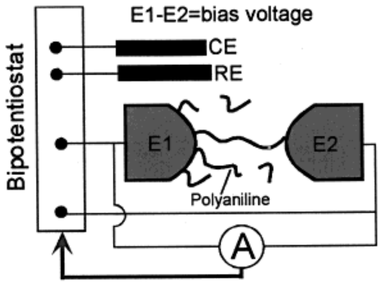

Figure 1. Schematic sketch of the formation of a conducting polymer nanojunction.

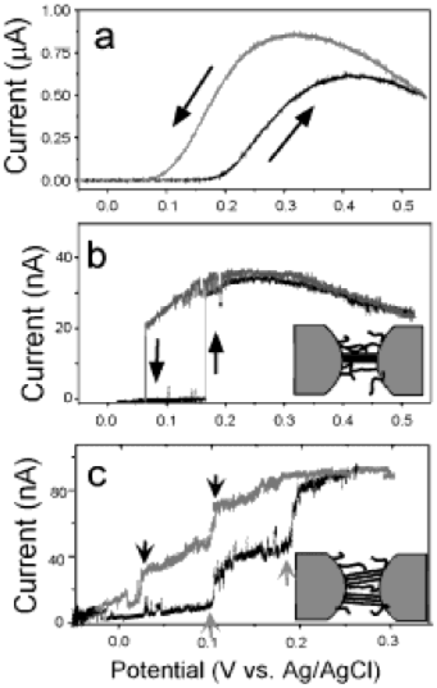

Figure 2. Charge transport current vs electrochemical potential for polyaniline nanojunctions with two Au nanoelectrodes separated with ~50 nm (a) and ~1 nm (b and c). The bias voltage between the nanoelectrodes in each case is 20 mV.

After forming a small gap, we deposit polyaniline onto the nanoelectrodes by sweeping the electrochemical potential between 0.15 and 0.75 V (vs Ag/AgCl) in 30 mM aniline + 0.5 M Na_2SO_4 (pH 1).[7] When the growing polyaniline bridges the gap, the current increases sharply across the gap, which prompts an immediate stop of the deposition process. We then replace the aniline solution with bare supporting electrolyte and study the conductance of the polyaniline nanojunction as a function of electrochemical potential.

For relatively large junctions in which polyaniline is sandwiched between two nanoelectrodes separated with 20−80 nm gap, the current increases smoothly and reaches a maximum near 0.4 V, as the polymer is switched from insulating to conducting states (Figure 2). Although the polymer can be reversibly switched between conducting and insulating states, a large hysteresis is apparent, which has been attributed to structural relaxations.[8]

The electrochemical potential-dependent charge transport behavior described above is similar to that of the bulk polymer

---

[†] Florida International University.

[‡] Motorola Labs.

[1] (a) Fan, F.-R. F.; Bard, A. J. *Science* **1997**, *277*, 1791−1793. (b) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279−9280. (c) Feldheim, D. L.; Keating, C. D. *Chem. Soc. Rev.* **1998**, *27*, 1−12.

[2] (a) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741−1744. (b) Schön, J. H.; Dodabalapur, A.; Bao, Z.; Ch., K.; Schenker, O.; Batlogg, B. *Nature* **2001**, *410*, 189−192. (c) Bartlett, P. N.; Astier, Y. *Chem. Commun.* **2000**, 105−112.

[3] Joo, J.; Long, S. M.; Pouget, J. P.; Oh, E. J.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1998**, *57*, 9567−9580.

[4] (a) White, H. S.; Kittlesen, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375−5377. (b) Jones, E. T. T.; Chyan, O. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5526−5528.

[5] Li, C. Z.; He, H. X.; Tao, N. J. *Appl. Phys. Lett.* **2000**, *77*, 3995−3997.

[6] He, H. X.; Li, C. Z.; Tao, N. J. *Appl. Phys. Lett.* **2001**, *78*, 811−813.

[7] Genies, E. M.; Tsintavis, C. *J. Electroanal. Chem.* **1985**, *195*, 109−128.

[8] Otero, T. F.; Grande, H.-J.; Rodriguez, J. *J. Phys. Chem.* **1997**, *101*, 3688−3697.

10.1021/ja016264i CCC: $20.00

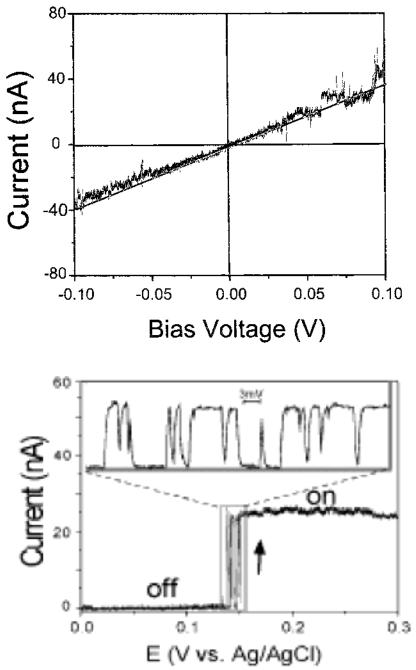

Figure 3. Top: $I-V$ characteristic of a Au-polyaniline-Au nanojunction. Bottom: Fluctuations near the onset of a switching from insulating to conducting states. The asymmetry of the fluctuation plateaus shown in the inset is due to the response of the Keithley 617 electrometer (slower than the STM preamplifier).

materials.[4] However, reducing the junction to a few nanometers, the smooth transition is replaced by an abrupt switching (Figure 2b). Below $\sim$0.15 V, the polymer is in the insulating state and the current is essentially the leakage current ($<$0.05 nA). Increasing the potential to $\sim$0.15 V, the current jumps suddenly by several orders of magnitude to $\sim$30 nA. The potential change required to switch the nanojunction from insulating to conducting states is $<2\ \mu$V, at least 5 orders of magnitude sharper than that of the larger junctions. The estimated conductivity of the polymer in the nanojunction is 10$-$100 S/cm. However, because of the unknown potential difference at the Au$-$polyaniline interfaces, the estimate serves only as a rough lower limit. Decreasing the potential, the current jumps back to zero but at a more negative potential. This hysteresis is similar to that of the bulk materials.

The switching between insulating and conducting states takes place in several abrupt steps in many samples. Figure 2c shows a two-step switching process. While the process is reversible, the hysteresis is as big as that in the single step switching. These steps are not due to conductance quantization[9] because the step height is several orders of magnitude smaller than the conductance quantum, $2e^2/h$. The switching is due to polyaniline because without it the current stays on the level of pA and independent of the electrochemical potential.

We have measured the current through the nanojunction held at the conducting state as a function of the bias voltage between the two nanoelectrodes (Figure 3, top). Although the current is roughly linear as we expect for a metallic phase, a deviation from the simple ohmic behavior is also apparent. The deviation may be due to electric field induced change in the conductivity, which has been observed in bulk material.[3]

Another interesting observation is noise near the edge of the insulating$-$conducting switching (Figure 3, bottom). Zooming in the noise resolves abrupt fluctuations of the conductance between two plateaus, corresponding to the insulating and conducting states. These fluctuations may be due to the fluctuations in the electrochemical potential. Because the switching is extremely sharp, a small fluctuation in the electrochemical potential is enough to switch the states of the polymer nanojunction.

It is tempting to attribute the stepwise changes in the charge transport to the individual polymer strands that are switched between insulating and conducting states. However, this interpretation would mean a small hysteresis because hysteresis is related to structural relaxations involving interchain interactions. We attribute the abrupt switching to a single nanocrystalline domain in which the individual polymer strands undergo insulator$-$conductor transition *collectively* (insets of Figure 2). This interpretation is in accordance with the growing evidence emphasizing the important role of the interchain coupling in conducting polymers.[10,3] It explains also the large hysteresis and is consistent with the fact that polyaniline materials consist of conductive domains of a few nanometers. According to this model, a nanojunction dominated by a single nanocrystalline domain switches between insulating and conducting states in a single step. When several domains are present in a nanojunction, the switching occurs in multiple steps as each domain is successively switched. The steps are smeared out in larger junctions that consist of many domains. A complete understanding of this phenomenon requires further studies, including the polymer$-$electrode interfaces.

The switching between insulating (off) and conducting (on) states is faster than 0.01 ms (limited by the response of our preamplifier), much faster than bulk polymers. A systematic study of the switching rate is currently hindered by the bandwidth of the preamplifier needed for measuring the small current. The insulator$-$conductor transition is triggered by oxidation and reduction of the polymers, involving various structural relaxations that place an intrinsic limit on the switching rate of the polymer switches. The structural relaxations include conformational change of each polymer chain involving bond angles and lengths and diffusion of counterions in to and out of the interchain free volume.[8] The relative importance of these processes is still a subject of debate, but it is clear that the rates of the processes increase as the size of the polymer materials decreases.

Another important parameter in terms of device applications is power gain, defined as the ratio of the output power to the power needed to switch a device on. The power change between off and on states is 4×10^{-10} W, and the needed power is $\sim 10^{-16}$ W, estimated from the required increase in the electrochemical potential and the corresponding current flow. So the minimum power gain is $\sim 10^{6}$.

In summary, by reducing a polymer junction to the order of a few nanometers, we have observed an abrupt switching between insulating and conducting states, which is qualitatively different from that of the bulk materials. The experiment demonstrates a method for studying charge transport on a scale comparable to individual nanocrystalline domains, and much higher switching rate and power gain in terms of applications. The abrupt switching may be used to improve the sensitivity of chemical sensor applications.

Acknowledgment. We thank NSF(CHE-9818073) and AFOSR-(F49620-99-1-0112) for financial support.

JA016264I

---

[9] (a) Wharam, D. A.; Thornton, T. J.; Newbury, R.; Pepper, M.; Ahmed, H.; Frost, J. E. F.; Hasko, D. G.; Peacock, D. C.; Ritchie, D. A.; Jones, G. A. C. *J. Phys. C* **1988**, *21*, 209$-$214. (b) Wees, B. J. v.; Houten, H. v.; Beenakker, C. W. J.; Williams, J. G.; Kouwenhowen, L. P.; Marel, D. v. d.; Foxon, C. T. *Phys. Rev. Lett.* **1988**, *60*, 848$-$850.

[10] Wang, Z. H.; Li, C.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. Lett.* **1991**, *66*, 1745$-$1948.