

Discrete conductance switching in conducting polymer wiresH. X. He, X. L. Li, and N. J. Tao*
*Arizona State University Tempe, Arizona 85287, USA*L. A. Nagahara, I. Amlani, and R. Tsui
Physical Sciences Research Laboratories, Motorola Labs 7700 S. River Parkway, Tempe, Arizona 85284, USA
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Charge transport in conducting polymers (polyaniline and polypyrrole) bridged between two gold nanoelectrodes separated with a nanoscale gap (varying from ~ 1 nm to a few tens of nm) was studied by controlling the polymer redox states electrochemically. In sharp contrast to the macroscopic samples, the conductance switches abruptly between insulating (off) and conducting (on) states like a telegraphic signal. The time durations of the on and off states depend on the potential of the nanoelectrodes, indicating the important role of the redox states in the signal. We attribute the telegraphic signal to the fluctuation between the insulating reduced state and conducting oxidized state of the polymer, which rises as electrons trap into the oxidized state and escape from the reduced state.

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I. INTRODUCTION

The promise of building electronic devices using molecules has triggered a recent surge of interest in studying electron transport through individual molecules.¹⁻⁸ Conducting polymers are attractive materials for molecular electronics, both as active elements and as molecular wires for interconnecting active elements, because of their unique properties. For example, the conductivities of many conducting polymers can be flexibly varied over many orders of magnitude by controlling their redox states electrochemically. Bulk conducting polymer materials have been extensively studied and used for various devices, from field effect transistors to biosensors.^{9,10} However, a direct study of charge transport through a single conducting polymer strand has been technically challenging, which has been a serious hindrance for a complete understanding of the materials and for molecular electronics applications using the polymers. Electron transport properties of polymer materials have been studied in the nanochannels of zeolite,¹¹ in solvents¹² and between microfabricated electrodes.¹³ In all these approaches, the measurements are associated with a large ensemble of polymer strands. We have recently demonstrated a method to study charge transport through a small amount of polymer strands bridged across two nanoelectrodes separated with a few nm wide gap.¹⁴

In this work, we report on a two-level telegraphic switching between conducting (on) and insulating (off) states in a conducting polymer wire (polyaniline and polypyrrole) bridged across two gold nanoelectrodes. We have studied the switching by controlling the redox state of the polymer with the potential of the nanoelectrodes, and the separation between the nanoelectrodes (from ~ 1 nm to a few tens of nm). At negative potentials, the polymer is in the insulating reduced state and the conductance is always off. Increasing the potential, it switches abruptly between the on and off states. At high potentials, the polymer is in the oxidized state and the conductance stays predominantly in the on state. We suggest that the telegraphic switching to a fluctuation in the

redox states of individual polymer wires as electrons trap in or escape from the polymers.

The on-off switching is likely related to the origin of the $1/f$ noise widely observed in polymer-based electronic and optoelectronic devices.^{15,16} In terms of chemical or biological sensor applications,^{17,18} if one wants to improve the sensitivity and response time by decreasing of the size of redox polymer sensing element (increasing the surface to volume), the telegraphic switching places a possible fundamental limit in the sensitivity of the sensor applications.

II. EXPERIMENTAL METHOD

Studying redox molecules sandwiched between two electrodes with the scanning tunneling microscope (STM) has been proposed theoretically^{19,20} and performed experimentally.²¹⁻²³ The STM approach allows one to image the individual molecules before and after measurements but it lacks long-term stability that makes many detailed studies difficult or even impossible. In the present work, we used a pair of nanoelectrodes separated with a gap of a few nm [Fig. 1(a)].

The nanoelectrodes were fabricated electrochemically using conductance quantization and electron tunneling as feedback signals. A detailed description of the fabrication technique was given elsewhere,^{24,25} but here we provide a brief summary. We started with an array of ten pairs of Au nanoelectrodes on oxidized Si substrate using electron beam lithography.²⁶ The initial separation between two nanoelectrodes in each pair varied from 20 to 60 nm. We then further reduced the gap by electroplating Au onto the nanoelectrodes which was controlled with a homemade bipotentiostat. We stopped the electroplating process once a certain amount of tunneling current (0.1 pA to a few pA for a bias voltage of 0.1 V) began to flow across the nanoelectrodes. In order to precisely measure the tunneling current, we reduced the leakage current due to ionic conduction well below 1 pA by coating the nanoelectrodes with SiN. We estimated the gap width using the exponential dependence of the tunnel con-

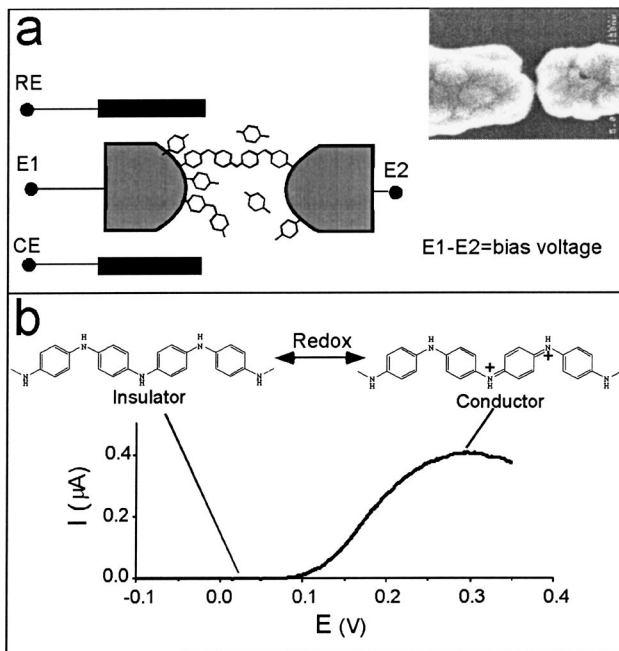


FIG. 1. (a) Scheme of the experimental setup. A pair of Au nanoelectrodes with a gap of 20–80 nm was fabricated with electron beam lithography. The gap was then reduced to as small as 1 nm (inset) by a controlled electrochemical deposition of Au onto the nanoelectrodes. Polyaniline was deposited electrochemically onto the nanoelectrodes to form a Au-polyaniline-Au nanojunction until a current begins to flow between the two nanoelectrodes. (b) Current flow through a bulk polyaniline wire as a function of potential.

ductance G on the gap width d , or $G = G_0 \exp(-\beta d)$. We determined that the decay constant, $\beta \sim 10 \text{ nm}^{-1}$, using a STM measurement in the similar environment.²⁷ To determine the absolute gap width, one would need to define the zero gap width. Here we assumed that zero gap occurred when the tunnel conductance was $G_0 = 2e^2/h$, corresponding to the contact of a single Au atom between two electrodes.

We bridged the gap with conducting polymer by cycling the potential of the nanoelectrodes in 0.25 M NaHSO₄ containing 50 mM aniline.^{10,13,28} The potential cycling served two purposes: polymerized aniline into polyaniline and deposited it onto the nanoelectrodes. Once polyaniline bridged the gap, the current between the nanoelectrodes jumped up by 2–3 orders of magnitude and the potential cycling was stopped immediately to minimize the amount of the deposited polyaniline. The number of potential cycles required to bridge the gap varied from a few to a few tens, which correlates roughly with the gap width. In order to study polyaniline-electrode interface effects, we coated the Au electrodes in some measurements with a 4-aminothiophenol monolayer so that aniline can covalently bind to the NH₂ group of the 4-aminothiophenol.^{29,30} Polypyrrole junction was obtained following the same procedure except that the electrolyte is 50-mM pyrrole monomers in 0.1 M KNO₃ (pH=2).

We studied the charge transport of the polymer wires as a function of the potential of the nanoelectrodes with respect to a reference electrode (Ag wire) in the electrolyte. The Ag

reference electrode was calibrated against the more frequently used Ag/AgCl reference electrode. We controlled potential with a homemade bipotentiostat using a Pt wire as counter electrode. We measured the conductance of the polymer wires by applying a small dc bias voltage (20 mV) between the two nanoelectrodes and recording the current using an electrometer (Keithley, model 617 electrometer). The current and potential were recorded with a digital oscilloscope (Yokogawa DL708). To improve the signal to noise ratio, we used also an ac technique in some measurements, in which an ac bias voltage (2-mV amplitude and 570 Hz) was applied between the two nanoelectrodes and the corresponding current modulation was converted to voltage with a current preamplifier and then sent to lock-in amplifier to determine the conductance. The ac technique did provide better signal to noise ratio, but the bandwidth was narrower than the dc measurement.

III. RESULTS AND DISCUSSIONS

Figure 1(b) shows the dependence of the conductance on the potential for a bulk polyaniline sample, prepared by depositing a large amount of polyaniline between two Au electrodes separated with a gap of ~ 60 nm. The dependence agrees well with the previously reported data.¹³ At very negative potentials, the polymer is in the insulating reduced state. Increasing the potential, the conductance increases smoothly as the polymer becomes oxidized. The removal of electrons from the polymer during the oxidation induces a structural distortion in the polymer chains and results in the formation of polaron (bipolaron) states located in the lowest-unoccupied–highest occupied molecular-orbital gap, which is the origin of high conductance in polyaniline and other conducting polymers. The maximum conductance occurs approximately when one electron is removed from every two monomers. Further oxidation results in a decrease in the conductance and may cause degradation of polyaniline, which was avoided by staying away from the high potential regime. If one holds the potential in the conductive regime (e.g., between 0.1 and 0.3 V), the conductance is essentially constant with some small random noise. The potential dependence of the conductance for bulk polypyrrole samples is similar except that the maximum conductance is ~ 0.2 V more negatively than that of polyaniline.

In order to study electron transport through a single or a few polymer strands, we used the nanoelectrodes separated with a smaller gap (1–20 nm) and carefully controlled the process of bridging polyaniline (polypyrrole) across the gap by monitoring the current between the nanoelectrodes. Once the current started to flow, we immediately stopped the polymer deposition process. It typically took only a few potential cycles to bridge polyaniline across a few nm gap. Holding the potential in the conductive regime, the conductance of these samples tends to switch randomly between a fixed value (on) and zero (off), like a telegraphic signal [Fig. 2(a)], which is in sharp contrast to that of the bulk samples. The measured switching is $\sim \mu\text{s}$, the time response limit of the current amplifier used in the measurement, so the actual switching rate is probably much faster. The time durations in

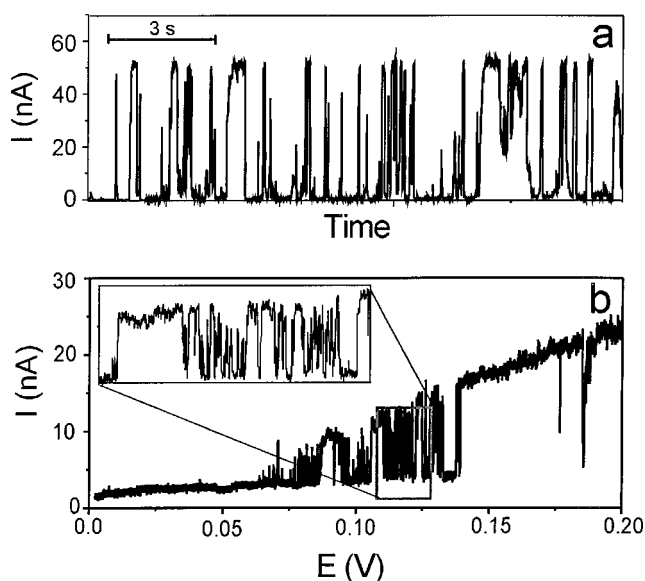


FIG. 2. (a) On-off random switching in the conductance of polyaniline (potential 0.2 V). (b) The dependence of the on-off switch on the potential of the nanoelectrodes. The inset shows more clearly the on-off switching.

the on and off states vary from μs to many seconds. The telegraphic switching is not sensitive to the applied bias voltage, which rules out possible roles played by electromigration. The observed conductance switching is indeed due to electron transport through polymers because it can be reversibly switched on and off near the potentials where the insulator-conductor transitions of polyaniline and polypyrrole take place (we will return to this). Furthermore, we performed the same measurement in the electrolyte containing no monomers and also in the electrolyte containing monomers but without polymerization. We found in each case, the current is always below ~ 1 pA, the leakage current, which rules out the possibility of monomers and ions in the gap as the origin of the measured conductance.

A random on-off switching in STM apparent height has been recently observed in phenylene-ethynylene adsorbed on an electrode and attributed to a random conformational change of a single molecule.⁶ In the present system, the on-off switching can be controlled by the redox state of the polymer with the potential of the nanoelectrodes. Figure 2(b) shows the conductance switching in a polyaniline wire as a function of the potential. At low potentials, the conductance is always off as the polymer is in the insulating reduced state. Increasing the potential causes partial oxidation of the polymer, and the conductance switches on abruptly. But instead of staying on the conductive state, it usually switches back and forth between the on and off states. The time ratio of the on- to off-states increases as the potential. At high potentials, the polymer predominately stays in the on state with only occasionally fluctuations to the off state then returning to the on state.

We have observed, in many samples, a multilevel switching between several discrete conductance values. The samples that exhibit this multilevel switching tend to require more potential cycles to bridge the gap, thus corresponding

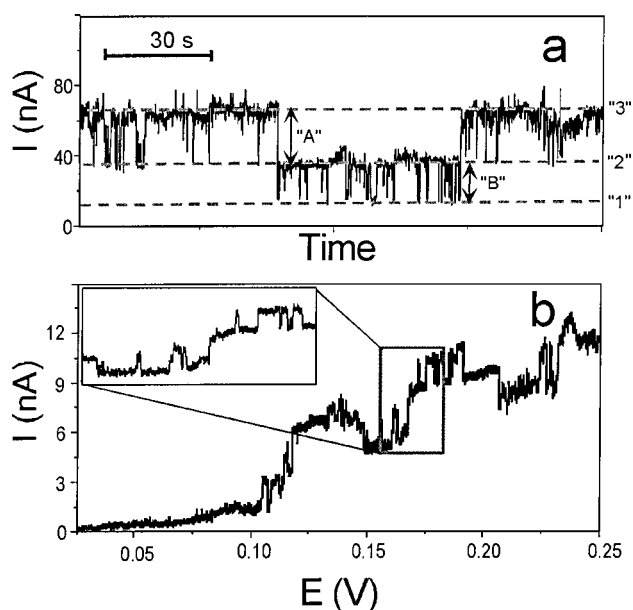


FIG. 3. (a) A random conductance switching between multiple discrete levels in a polyaniline wire (potential 0.2 V). (b) The dependence of the polyaniline switching behavior on the potential of the nanoelectrodes.

to more polymer strands deposited in the gap. Figure 3(a) shows a three level switching. In the beginning, the conductance switches rapidly between level 3 and level 2. At a certain time (arrow), it switches to level 1 and fluctuates between level 2 and level 1. Then at a later time, it switches back to level 3 and resumes the fluctuation between level 3 and level 2. Like the simple on-off switching, the multilevel switching can also be controlled by the potential. Figure 3(b) shows the conductance as the potential swept from negative to positive values. At very negative potentials, the polymer is in the insulating reduced state. As the potential increases, the conductance switches on and off between multiple discrete levels, and both the time duration and the conductance of the on-state increases. We have performed the experiment using electrodes separated with different gap widths and observed the telegraphic switching using gaps as large as ~ 20 nm. The telegraphic switching typically involves many levels and the conductance difference between two adjacent levels is much smaller. Further increasing the gap to the order of 50–100 nm, the conductance becomes smooth and indistinguishable from the measurements performed with macroscopic electrodes. The observation of the telegraphic signal in experiments with large gaps rules out the accidental connection between the electrodes.

We have studied the conductance of the polypyrrole wire and found a similar telegraphic switching (Fig. 4). The transition potential between the insulating and the conducting states for polypyrrole is somewhat more negative than that of polyaniline, which results in shift in the conductance vs. potential curves towards negative potential. Another difference between the two polymers is the reversibility of the switching behavior. The polyaniline wire can be switched back and forth between insulating and conducting states for many cycles as long as the potential is not high enough to overoxi-

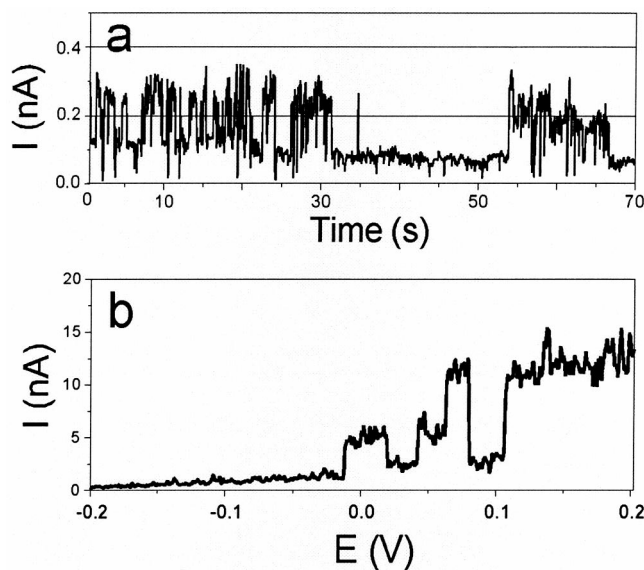


FIG. 4. (a) A random conductance switching between multiple discrete levels in a polypyrrole wire (potential 0.1 V). (b) The dependence of the polypyrrole switching behavior on the potential of the nanoelectrodes.

dize the polymer. In contrast, the conductance of the polypyrrole wire decreases as we repeatedly switch it between insulating and conducting states. This difference may reflect that the fact that polypyrrole is less stable than polyaniline.

An obvious question arises from the above observations: Is the on-off telegraphic switching the act of many polymer strands (chains) or a single strand? If it involves many strands in parallel, the abrupt switching means that all the strands switch on and off *collectively*.¹⁴ This is possible only if the polymer strands in the gap form a crystalline-like bundle such that the individual strands in parallel can interact with each other strongly. Statistically, a single strand crosses the narrow gap first seems to be much more likely than multiple strands in a bundle cross the gap simultaneously. Another possibility is to involve many strands in series, which gives rise to an on-off switching whenever the interchain hopping is disrupted or activated by a conformational change. This is not likely because our electrode spacing is often only large enough to fit a very short strand (a few monomers), which should be normal to the electrode surfaces when it binds covalently to the aminothiophenol.^{29,30} The interchain mechanism involving conformation changes cannot easily explain the strong dependence of the on/off switching on the potential. Finally, the interchain hopping is widely believed to conduct electricity much less effectively than that along the chains (strands).^{31–33} So even if a number of strands are deposited randomly in the gap, current flow through a whole strand (shortest one) is like to dominate the measured conductance.

Based on these considerations and more evidence presented below, we attribute the on-off telegraphic switching to the act of a single polymer strand and multilevel switching to the act of several individual polymers. We note that while this simple model explains all the observed facts, a direct proof is not yet possible. The typical current of the on-state is

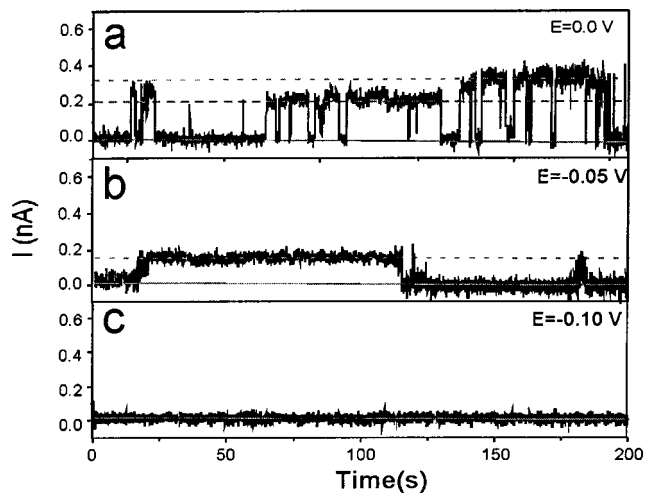


FIG. 5. A multiple level conductance switching at various potentials. At high potentials, the conductance fluctuates between several levels. Decreasing the potential, a single two level on-off switch is left as the rest are permanently shut off. At more negative potentials, the conductance is zero.

on the order of a few tens of nA for a small gap (\sim nm). If we take the conductivity data of polyaniline films,^{9,34} the estimated current for a single strand (using a cross sectional area of 0.3 nm^2 and length of 2 nm) is on the same order of magnitude. This estimate is rather crude because the published data is averaged over many strands involving interchain hopping, and the conduction mechanism in our system can be quite different.

If the multilevel switching is indeed due to individual polymer strands, we expect that the on-off switches turn off successively at negative potentials as each individual strand is reduced to the insulating state. This behavior was observed and an example is shown in Fig. 5 for polyaniline. At high potentials, the conductance fluctuates between multilevels. Lowering the potential to 0 V, only two independent on-off switches left, one with a on current of ~ 0.35 nA, and the other one ~ 0.2 nA. This is because the probability of a polymer chain in the oxidized (conducting) state decreases with the potential. Further lowering the potential to -0.05 V, only a single on-off switching is left with all others being turned off. At -0.1 V, the last on-off switch is also turned off. This experiment shows also that even if multiple strands are present in the gap, we can study the conductance of a single strand by switching the rest off. While the example in Fig. 5 shows multiple strands switch independently, we have also observed correlated switching behaviors.³⁵ One such example is given in Fig. 2(a), which shows that polymer strand B can switch off only when A is off.

The next question is: what causes the switching? Telegraphic signal has been observed in the conductance of other nanostructures, such as metallic nanoconstrictions^{35–37} and nanoscale MOSFET.³⁸ They are usually less than 1% in amplitude superimposed on a large conductance, and attributed to the trapping of conduction electrons in *single* defects. In the present system, the conductance is either on or completely off. If extending the defect-trapping model to the present system, then a single defect must be able to com-

pletely block the charge transport. This is possible only if the conductance is dictated by a single polymer strand so that the presence of a defect state in the strand can control the conductance of the entire chain.

An obvious place to look for defects is the interface between the polymer and the nanoelectrodes. The importance of molecule-electrode interface in the conductance of molecular wires has been discussed.³⁹ Indeed, even a simple fluctuation in the contact geometry between the polymer and the Au electrodes may lead to an on-off switching in the measured conductance. In order to examine this possibility, we have modified the Au electrodes with 4-aminothiophenol for polyaniline wires. It has been shown that the thiol group binds tightly to Au via the S-Au bond, and the NH₂ group can form a covalent bond to polyaniline.^{29,30} The on-off switching exists regardless of the modification of the electrode surfaces, so the interface is unlikely the cause of the telegraphic switching. The interface model has also difficulty explain the dependence of the telegraphic signal on the potential.

The strong potential dependence leads us to believe that the conductance switching is due to a fluctuation in the redox states of the polymer. Adding an electron to or removing an electron from a redox molecule is known to accompany a large conformational relaxation, including structural distortion (bond angle and length) in the molecule and polarization of the surrounding solvent molecules.⁴⁰ The importance of conformational changes in the conductance of molecular wires has been recognized by several groups.^{41–43} The strong electron-conformation coupling means that a fluctuation in the conformation can cause a large shift in the electronic energy levels of the polymer.^{19,40,44} In the reduced state, the highest occupied state of the polymer is well below the Fermi levels of the electrodes and the conductance is off. Increasing the electrode potential moves the Fermi levels closer to the occupied state, and a conformational fluctuation becomes enough to shift the occupied state to the Fermi levels (Fig. 6). The electrons in the occupied state can then transfer to the electrodes and the polymer is consequently oxidized. The oxidation of the polymer transforms it to the conducting state and switches the conductance on. The conductance stays on until an electron traps in the oxidized state and the polymer returns to the insulating reduced state. This model explains naturally the dependence of the on-off conductance switching on the potential of the electrodes. In terms of the defect-trapping model, we may regard the oxidized state as a “defect” state and trapping electrons in it transforms the polymer wire to the insulating reduced state

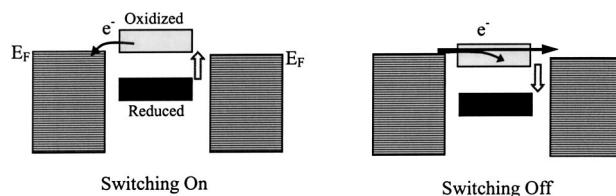


FIG. 6. Schematic sketch of redox fluctuation-induced conductance switching model. When electrons escape from the reduced (insulating) polymer, the polymer becomes oxidized (conducting) and the conductance switches on. When conduction electrons trap in the oxidized states, the polymer becomes reduced and the conductance switches off.

and thus switching off the conductance. For bulk conducting polymer materials, small ions in the electrolyte can act both as counter ions and as dopants. Because the oxidation and reduction always accompany redistributions of the counter ions, fluctuations in the redox state and in the counter ion distribution are closely related.

Although the above model provides a qualitative explanation of the experimental data, a number of questions remain to be addressed. For example, to what extent can one use the polaron or bipolaron descriptions developed for bulk polymer materials to the present system that consists a few short strands of polymers? A complete understanding of the process clearly requires further theoretical and experimental efforts.

IV. CONCLUSIONS

In conclusion, we have studied charge transport in polyaniline strands bridged across two gold nanoelectrodes separated with a nm-scale gap. We observed a telegraphic on-off switching in the conductance that can be controlled by the redox states of the polymer with the potential. When we increase the amount of polymer deposited in the gap, the simple two-level switching is first replaced by a multiple-level switching and then disappears into the background noise. We attribute the on-off switching to the fluctuation between the conducting oxidized state and insulating reduced state of the polymer as electrons trap in and escape from the polymer.

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*Corresponding author. Email address: nongjian.tao@asu.edu.

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