Electrical Transport and Chemical Sensing Properties of Individual Conducting Polymer Nanowires

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Supporting Information

Nanowire Synthesis. The multi-segmented nanowire samples were synthesized by sequential deposition in the alumina membrane templates. A thin layer of silver (200 nm thickness) was first evaporated onto one side of the alumina membranes (Anodisc 25 with 0.2 m pore diameter, commercially available from Whatman). The silver layer was then used as part of the working electrode for electrodeposition. The first segment of gold was deposited galvanostatically at -1.75 mA for 15 minutes from a cyanide-based gold plating solution (Orotemp 24, commercially available from Technic Inc.). The conducting polymer segment in the middle was anodically electrodeposited in a three-electrode cell. The PEDOT/PSS segment was polymerized from a solution of 0.05 M 3,4-ethylenedioxythiophene, 0.1 M PSS in 1:1 v/v water/acetonitrile at 1 V vs. a saturated calomel electrode for 14 minutes. The PEDOT/ClO_4 segment was polymerized from a solution of 0.01 M EDOT, 0.1 M lithium perchlorate in acetonitrile at 1.4 V vs. a Ag/AgCl electrode for 7 minutes. The gold segment on top of the polymers was synthesized in two steps. The first step is the electroless deposition of gold with a slightly modified version of a procedure[1] reported by Menon and Martin. Briefly, the membrane was successively submersed into 25 mM $SnCl_2$ and 70mM trifluoroacetic acid in 50:50 methanol/water (3

minutes), 30 mM $AgNO_3$ and 300 mM aqueous ammonia (2 minutes), and a 1:1 v/v mixture of a 20 times diluted Oromerse (from Technic Inc.) solution and a solution of 1.25 M formaldehyde and 0.254 M Na_2SO_3 followed by adjusting the pH to 6 with 0.5 M sulfuric acid (24 hours). The second step is the electroplating of gold from Orotemp 24 (Technic Inc.) at a constant current of -1.75 mA for 30 minutes in order to elongate the relatively short gold end obtained in the electroless deposition step.

De-doping of PEDOT/ClO_4 nanowires. The electrochemical de-doping of PEDOT/ClO_4 was conducted in a three electrode cell containing the PEDOT/ClO_4 nanowire, which was connected to the working electrode lead of an EG&G Princeton Applied Research 363 Potentiostat. A platinum counter electrode and a Ag/AgCl reference electrode were also placed in the cell. The nanowire was aligned in the four-point measurement test bed by dielectrophoretic assembly as described previously.[12] One of the two gold metal pads that contacted the nanowire was wire bonded to one pin of a socket chip This pin was connected to the working electrode of the potentiostat. A glass tube was placed over the nanowire and 0.1 M $LiClO_4$ in acetonitrile was used as electrolyte. The potential applied to the nanowire was -2 V and was held constant for about 10 min. The sample was then rinsed successively with acetone, isopropanol and de-ionized water and air-dried.

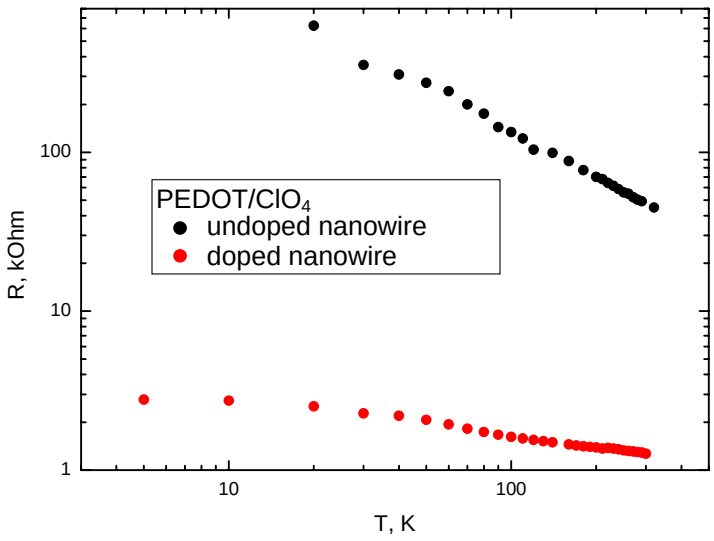

Figure S1. Comparison of the low bias resistance vs. temperature of doped and de-doped PEDOT/ClO_4 nanowires.

Transport Measurements. Temperature dependent electrical transport experiments were performed in a Lake Shore cryogenic probe station (5-300 K) under high vacuum conditions using an Agilent 4155C Semiconductor Parameter Analyzer. The nanowire resistance was measured by scanning over a +/- 1 V range. The resistance was calculated as the ratio of the voltage between the inner leads divided by the current measured at the outer leads. At temperatures below 30K, where the i-V curves were non-linear, the resistance was calculated from the slope of the linear part of the i-V curve near zero current.

For both PEDOT/PSS and PEDOT/ClO_4 five nanowires were measured. All five nanowires were measured at the same temperature within about 15 minutes. For the PEDOT/PSS nanowires, the sweep was done for two days with warming up to the room temperature overnight and no resistance change was observed. The time intervals between measurements on a given nanowire were irregular and no effects of possible time drift were detected. Temperature hysteresis is usually accompanied by signal drift at a given temperature due to relaxation into an equilibrium state. Therefore, the absence of the time drift may be considered as evidence of the absence of a strong temperature hysteresis. For all nanowires, the resistance of the inner contacts was about one to two orders of magnitude higher than the two-point resistance through the outer contacts, but no nonlinear effects were observed except at low temperatures. For the PEDOT/ClO4 nanowires, the resistance sometimes exhibited irreversible jumps which we believe are due to mechanical movement of the wires. Taking into the account these jumps, all PEDOT/ClO_4 nanowires showed similar temperature dependences.

Microscopy. Optical images were obtained with a Zeiss Axiotech microscope equipped with a Sony DFW-X700 camera. Field emission scanning electron microscopy (FESEM) images were obtained with a JEOL JSM 6700L field emission scanning microscope. Transmission electron microscopy (TEM) images were obtained with a JEOL 1200 EXII at 80 kV accelerating voltage.

References

1. Menon, V. P.; Martin, C. R. *Anal. Chem.* **1995**, *67*, 1920.