

Electroactive Polymer Actuation at the Nanoscale

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Abstract - Nanoscale actuators are required for the development of nanorobots and other nanoelectromechanical systems (NEMS) of the future. Actuators based on electrochemically-induced volumetric changes in electroactive polymers (EAPs) have been demonstrated at the macro and microscales, and have been used for artificial muscles and other applications. Here we experimentally and quantitatively demonstrate for the first time that the fundamental phenomena underlying EAP actuation are still active at spatial scales below 100 nm. This opens new directions in nanorobot and NEMS research. Individual polypyrrole structures are investigated in this paper by using atomic force microscopy (AFM) with electrochemistry capabilities. Polypyrrole-based nanowires (~50 nm diameter, ~6 μm in length) and single-walled carbon nanotubes coated with a polypyrrole film ~125 nm thick both show actuation behavior. The nanowire dimensions change from ~2% to as much as ~35%. The single-walled nanotube-polypyrrole structures show a considerably lower percentage of dimensional change.

Keywords – Atomic force microscopy, electroactive polymers, nanoactuators, nanorobotics, polypyrrole.

I. INTRODUCTION

Controlled motion at the nanoscale poses difficult challenges in nanorobotics research. Nanoscale devices are needed for propelling nanorobots and for mechanically acting upon the robots' environment [1]. Electrochemically-induced volume changes of doped polypyrrole (PPy) films have been extensively studied for their actuation properties. Actuation has been demonstrated for millimeter-scale, free standing, conjugated polymer structures [2-4], which have been used as artificial muscles [5]. Bimorph microscale actuators have been fabricated by Jager and Smela's groups [6]: MEMS fabrication techniques have been used to grow a PPy film onto a thin gold support which acts as an electrode.

The key feature of the polymer that enables the motion of the microscale bimorph structure is the volume change brought about electrochemically by a change in oxidation state. The PPy either gains or loses an ionic species to maintain charge neutrality, as shown in Fig. 1.

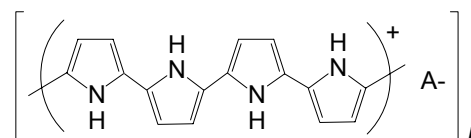
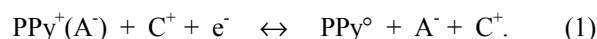
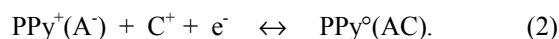


Figure 1. A general structure of polypyrrole doped with a counterion.

If the oxidized PPy structure is doped with small mobile anions (in natural oxidized state at 0V), the structure will decrease in volume as the anion (A^-) is expelled upon electrochemical reduction, as shown below



Volume increase in the PPy structure is observed upon electrochemical reduction if an immobile anion is used, since a cation (C^+) will be pulled into the structure from the surrounding electrolyte solution to balance the charge:



Electroactive polymers have shown great promise as actuator materials at the macro and microscales.

Here we demonstrate experimentally for the first time actuation properties for individual nanoscale and near-nanoscale PPy structures. The two different systems studied, as well as the methodology used for the measurements are introduced in Section II. Experimental results are presented Section III, followed by a discussion and conclusions in Section IV.

II. EXPERIMENTAL SYSTEMS AND AFM MEASUREMENTS

Two different architectures were prepared for actuation studies. Both structures used an immobile anion dopant in the fabrication process of the PPy. Therefore these structures were expected to increase in volume during electrochemical reduction.

A. 50 nm diameter PPy nanowires

Chemical polymerization within a track-etched polycarbonate membrane was used to fabricate polypyrrole *para*-toluene sulfonate PPy(pTS) nanowires with 50 nm diameter and ~6 μm length [7]. These nanowires were left intact within the polycarbonate membrane where gold was

subsequently evaporated onto one side of the membrane to serve as the working electrode during the electrochemical atomic force microscopy (AFM) experiment, which is described at the end of this section.

B. PPy-Coated Single-Walled Carbon Nanotubes

A highly dense network of single-walled carbon nanotubes were grown onto the surface of a silicon wafer sample. Gold electrodes were patterned onto this surface to electrically connect the carbon nanotubes and serve as the working electrode in both the PPy deposition process as well as the actuation experiments. Single-walled carbon nanotubes coated with polypyrrole dodecylbenzenesulfonate SWNT/PPy(DBS) were prepared by electrochemical deposition to form heterostructures having diameters ranging between 120 and 135 nm.

C. Electrochemical Atomic Force Microscopy

Actuation behavior of both the 50 nm PPy(pTS) nanowires and the SWNT/PPy(DBS) heterostructures were studied by electrochemical AFM in a electrolyte liquid environment. AFM topography images were taken for the PPy samples to compare the topography of the surface in the native oxidized state (0V), actuated state (reduced at -1V), then reoxidized to natural state (0V). For the case of the 50 nm PPy(pTS) nanowire sample, the topography of the protruding ends of the wires was measured to test actuation (Fig. 2). For the SWNT/PPy(DBS) heterostructure sample, the change in thickness of the SWNT/PPy(DBS) was measured.

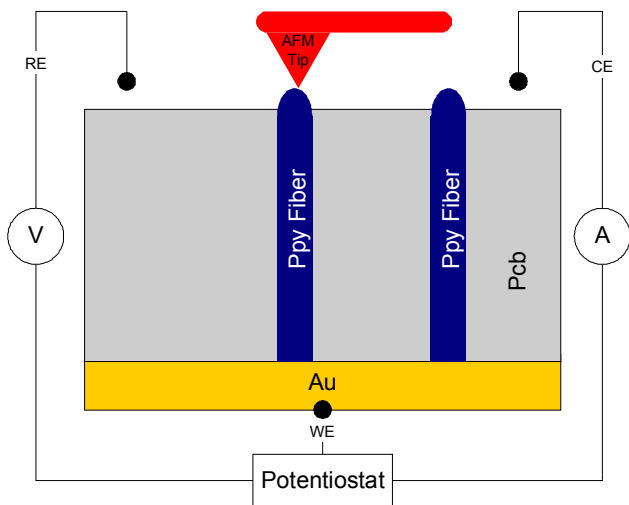


Figure 2. Schematic of 50 nm PPy(pTS) nanowire sample in the electrochemical AFM measurement. The tip and the entire sample are submersed in an electrolyte solution (not shown).

III. EXPERIMENTAL RESULTS

Initial actuation experiments for the 50 nm PPy(pTS) nanowire sample did not yield noticeable differences in topography as a function of oxidation state. Two-dimensional confinement seemed to inhibit the volume change ability of the

polymer. It was originally expected that the polycarbonate membrane structure would serve to support the nanowire, which would be free to swell out of the plane of the polycarbonate membrane. Chloroform was used to dissolve away a thin layer of the polycarbonate and expose a short segment of the PPy(pTS) nanowire. Subsequent electrochemical actuation tests showed a significant volume change response. Fig. 3 shows several nanowires (A, B, C, D) chosen for analysis. The length and width of the protruding parts of the PPy(pTS) nanowires were measured along orthogonal directions, with the length being the largest dimension of the feature, in the direction of its perceived axis. Tip effects were not taken into account, and therefore the length and width percent changes shown in the table are lower bounds on the actual values. Height data was obtained using cross section analysis at the highest point in of the feature. Dimensional changes were found to range from 1.45% to as much as 36.27%, as shown in Table I. This study indicates that only the exposed portion of PPy(pTS) is active for volume change behavior, and the majority of the six micron structure is inhibited through confinement.

TABLE I. ACTUATION ANALYSIS OF 50 NM DIAMETER PPy(pTS)

Nanowire	Initial Height (nm)	Height Change (%)	Initial Length (nm)	Length Change (%)	Initial Width (nm)	Width Change (%)
A	77.35	22.41	319	21.16	207.1	9.85
B	113.06	6.70	283.4	8.33	200.6	1.45
C	61.56	36.27	237.3	23.81	164.5	6.63
D	79	12.27	308.4	10.15	197.3	9.43

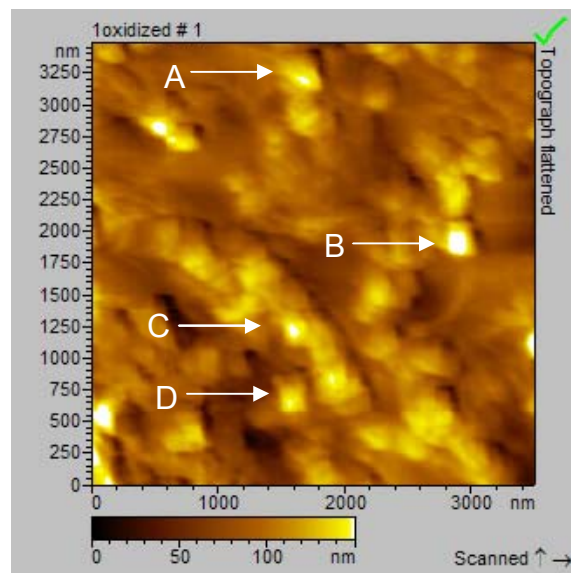


Figure 3. AFM topography image of 50 nm PPy(pTS) nanowires protruding from the background polycarbonate.

Fig. 4 is a representative topography image showing the gold working electrode as well as the SWNT/PPy(DBS).

Cross-section analysis of 25 locations of the SWNT/PPy(DBS) heterostructure was performed with the AFM for the same locations throughout the actuation experiment, and mean values and standard deviations were calculated from the 25 data points. Fig. 5 shows the mean thickness along with the standard deviation of one particular SWNT/PPy(DBS) structure in response to an electrochemical cycle. With a starting thickness of 132.4 ± 3.6 nm as measured by electrochemical AFM, the SWNT/PPy(DBS) is then subjected to a negative potential sufficient for polypyrrole reduction and results in the structure expanding to 135.5 ± 1.5 nm, a change of 2.3 ± 1.1 %. The thickness change was calculated by subtracting the before and after values obtained for each of the 25 cross-sections, averaging, and computing the standard deviation across the 25 data points. The expansion corresponds to the diffusion of sodium cations and their solvation shell water molecules into the polymer matrix. In order to oxidize the polypyrrole once again, the potential was increased from -1 to 0V, causing the tube thickness to shrink by 1.9 ± 0.9 % to 132.9 ± 1.3 nm. At the completion of one cycle, the SWNT/PPy(DBS) has nearly returned to its original thickness.

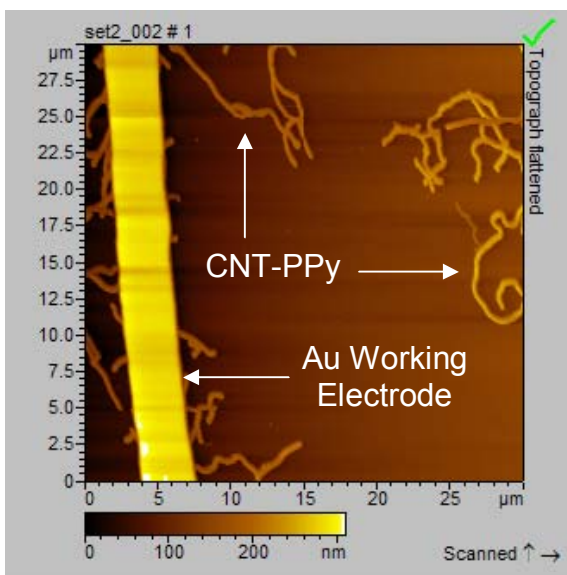


Figure 4. AFM topography image showing SWNT/PPy(DBS) connected to the gold working electrode. Other electrodes (not shown) are spaced at 20 micron intervals in order to maximize the number of electrically connected heterostructures.

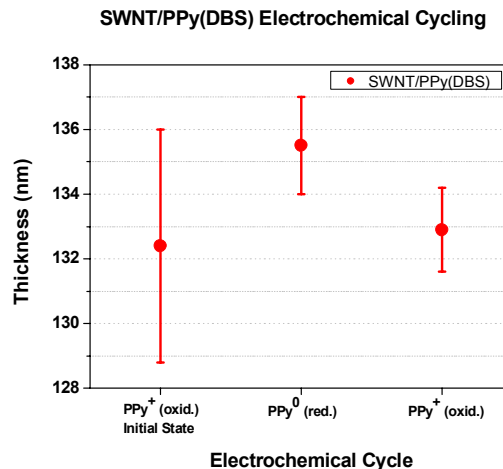


Figure 5. Thickness variations for a SWNT/PPy(DBS) undergoing an electrochemical cycle.

Thickness changes for the SWNT/PPy(DBS) sample were found to be more than an order of magnitude lower than the values reported by Smela and Gadegaard [8] for microscale films. In their work, the starting PPy(DBS) films were over 1500 nm thick and upon the first reduction cycle expanded by 61 % to 2450 nm. By comparison, our PPy(DBS) coatings were more than 12 times thinner and underwent a 25-fold smaller difference in expansion. One must also take into consideration the architectural differences between the two designs. Smela *et al.*'s work involved PPy(DBS) films generated in photolithographically-patterned well structures, while our design involved the formation of PPy(DBS) coatings onto 1-2 nm diameter SWNT structures.

IV. DISCUSSION AND CONCLUSION

The electrochemical switching ability of polypyrrole involves both charge and mass transfer and has been studied extensively [8-10]. Although work has been published on the synthesis and properties of various carbon nanotube-polypyrrole structures [11-14] very little, if any, has focused on the volume changes in polypyrrole associated with electrochemical cycling in these structures. By reducing the conducting polymer from its original oxidized state back to its neutral form, mass diffusion must occur in order to maintain charge balance. The relatively large sizes of *para*-toluene sulfonate or dodecylbenzenesulfonate anions within the polypyrrole structure force the smaller and more mobile sodium cations to diffuse into the polymer to maintain charge neutrality. Therefore, we expect during the polypyrrole reduction cycle a concomitant increase in the volume of the PPy, attributable to the insertion of sodium ions and their accompanying solvation shells into the polymer. Indeed, our results obtained from electrochemical cycling of both the 50 nm diameter PPy(pTS) nanowire as well as SWNT/PPy(DBS) support this mechanism.

In summary, we presented in this paper quantitative experimental results that show that the fundamental phenomena which underlie EAP actuation are still active at the nanoscale. Although much work is still needed before practical nanoactuators can be built based on the principles demonstrated here, we believe that a crucial first step has been taken in that direction. Nanoactuators operating in liquid environments may find important biomedical applications in the future.

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REFERENCES

- [1] A. A. G. Requicha, "Nanorobots, NEMS, and nanoassembly," *Proceedings of the IEEE*, vol. 91, pp. 1922-1933, 2003.
- [2] J. Ding, D. Z. Zhou, G. Spinks, G. Wallace, S. Forsyth, M. Forsyth, and D. MacFarlane, "Use of ionic liquids as electrolytes in electromechanical actuator systems based on inherently conducting polymers," *Chemistry of Materials*, vol. 15, pp. 2392-2398, 2003.
- [3] A. Della Santa, D. DeRossi, and A. Mazzoldi, "Performance and work capacity of a polypyrrole conducting polymer linear actuator," *Synthetic Metals*, vol. 90, pp. 93-100, 1997.
- [4] H. L. Wang, J. B. Gao, J. M. Sansiñena, and P. McCarthy, "Fabrication and characterization of polyaniline monolithic actuators based on a novel configuration: Integrally skinned asymmetric membrane," *Chemistry of Materials*, vol. 14, pp. 2546-2552, 2002.
- [5] E. A. Moschou, S. F. Peteu, L. G. Bachas, M. J. Madou, and S. Daunert, "Artificial muscle material with fast electroactuation under neutral pH conditions," *Chemistry of Materials*, vol. 16, pp. 2499-2502, 2004.
- [6] E. Smela, "Conjugated polymer actuators for biomedical applications," *Advanced Materials*, vol. 15, pp. 481-494, 2003.
- [7] J. M. Mativetsky and W. R. Datars, "Morphology and electrical properties of template-synthesized polypyrrole nanocylinders," *Physica B: Condensed Matter*, vol. 324, pp. 191-204, 2002.
- [8] E. Smela and N. Gadegaard, "Volume change in polypyrrole studied by atomic force microscopy," *Journal of Physical Chemistry B*, vol. 105, pp. 9395-9405, 2001.
- [9] E. Smela and N. Gadegaard, "Surprising volume change in PPy(DBS): An atomic force microscopy study," *Advanced Materials*, vol. 11, pp. 953-957, 1999.
- [10] M. F. Suárez and R. G. Compton, "In situ atomic force microscopy study of polypyrrole synthesis and the volume changes induced by oxidation and reduction of the polymer," *Journal of Electroanalytical Chemistry*, vol. 462, pp. 211-221, 1999.
- [11] J. H. Fan, M. X. Wan, D. B. Zhu, B. H. Chang, Z. W. Pan, and S. S. Xie, "Synthesis and properties of carbon nanotube-polypyrrole composites," *Synthetic Metals*, vol. 102, pp. 1266-1267, 1999.
- [12] Y. Z. Long, Z. J. Chen, X. T. Zhang, J. Zhang, and Z. F. Liu, "Electrical properties of multi-walled carbon nanotube/polypyrrole nanocables: percolation-dominated conductivity," *Journal of Physics D: Applied Physics*, vol. 37, pp. 1965-1969, 2004.
- [13] J. H. Chen, Z. P. Huang, D. Z. Wang, S. X. Yang, J. G. Wen, and Z. R. Ren, "Electrochemical synthesis of polypyrrole/carbon nanotube nanoscale composites using well-aligned carbon nanotube arrays," *Applied Physics A: Materials Science & Processing*, vol. 73, pp. 129-131, 2001.
- [14] J. H. Fan, M. X. Wan, D. B. Zhu, B. H. Chang, Z. W. Pan, and S. S. Xie, "Synthesis, characterizations, and physical properties of carbon nanotubes coated by conducting polypyrrole," *Journal of Applied Polymer Science*, vol. 74, pp. 2605-2610, 1999.