Actuation of polypyrrole nanowires

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Abstract
Nanoscale actuators are essential components of the NEMS (nanoelectromechanical systems)
and nanorobots of the future, and are expected to become a major area of development within
nanotechnology. This paper demonstrates for the first time that individual polypyrrole (PPy)
nanowires with diameters under 100 nm exhibit actuation behavior, and therefore can
potentially be used for constructing nanoscale actuators. PPy is an electroactive polymer which
can change volume on the basis of its oxidation state. PPy-based macroscale and microscale
actuators have been demonstrated, but their nanoscale counterparts have not been realized until
now. The research reported here answers positively the fundamental question of whether PPy
wires still exhibit useful volume changes at the nanoscale. Nanowires with a 50 nm diameter
and a length of approximately 6 μm, are fabricated by chemical polymerization using
track-etched polycarbonate membranes as templates. Their actuation response as a function of
oxidation state is investigated by electrochemical AFM (atomic force microscopy). An estimate
of the minimum actuation force is made, based on the displacement of the AFM cantilever.

(Some figures in this article are in colour only in the electronic version)
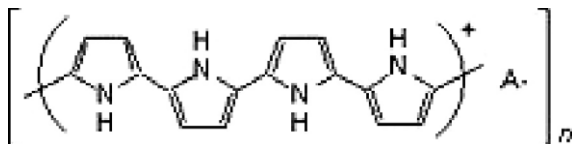
1. Introduction

Electrochemically induced volume changes of doped polypyrrole (PPy) films have been extensively studied. Actuation has been demonstrated for millimeter scale, free standing conjugated polymer structures [8, 6, 30] and for applications such as artificial muscles [23]. Miniaturization is expected to benefit performance, as discussed by Smela [26]. Bimorph microactuators have been fabricated by Jager's group, by using a MEMS (microelectromechanical systems) fabrication technique to create a PPy film attached to a thin support structure of gold, which can also act as an electrode [14, 15, 13, 12]. The key phenomenon that enables actuation of the microscale bimorph structure is the volume change brought about by an electrochemical change in oxidation state, in which the PPy ei-
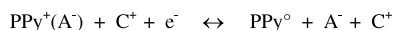
ther gains or loses an ionic species to maintain charge neutrality (see figure 1). In the case where the oxidized PPy structure is doped with small mobile anions (in natural oxidized state at 0 V), the PPy structure will decrease in volume as the anions (A$^-$) are expelled from the structure upon electrochemical reduction, as shown in scheme 1.

And for the case where the oxidized PPy is doped with larger immobile anions, the structure will swell upon electrochemical reduction as the cations (C$^+$) are pulled from the electrolyte solution into the PPy structure, as shown in scheme 2.

The volume change described in the above mechanism induces lateral stress on the adjacent support structure, resulting in motion. Smela and Gadegaard demonstrated volume changes for a rectangular stripe pattern (10 and
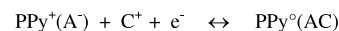
Figure 1. Structure of doped polypyrrole in its doped state at 0 V. The anion is present in the polymer matrix to maintain charge neutrality.

$$PPy^+(A^-) + C^+ + e^- \leftrightarrow PPy^\circ + A^- + C^+$$

Scheme 1. Reversible redox reaction of doped PPy having a mobile anion which can easily leave the PPy polymer matrix.

$$PPy^+(A^-) + C^+ + e^- \leftrightarrow PPy^\circ(AC)$$

Scheme 2. Reversible redox reaction of doped PPy having an immobile anion such that a cation from the solution will enter and leave the polymer matrix in order to maintain charge neutrality.
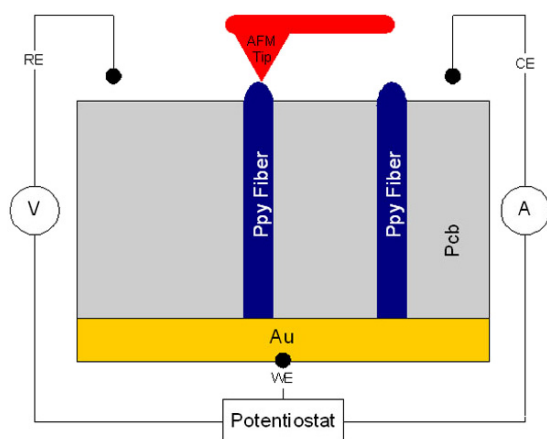
We have successfully fabricated 50 nm diameter polypyrrole nanowires doped with p-toluenesulfonate PPy(pTS) for which *in situ* actuation was demonstrated by using an AFM having electrochemistry capabilities. Our research is motivated by the goal of developing actuators for nanorobotic and nanoelectromechanical system (NEMS) applications of the future. Nanoscale actuators will be important components of nanorobots and other NEMS, and PPy nanowires are promising candidates for such actuators. PPy-based actuators are well suited for operations in liquid media, which are especially interesting for biological systems, where nanorobots and NEMS are likely to find major applications. Robotic applications of electroactive polymer actuators at the microscale have been reported in [12]. We are interested in investigating similar applications, but at the nanoscale.
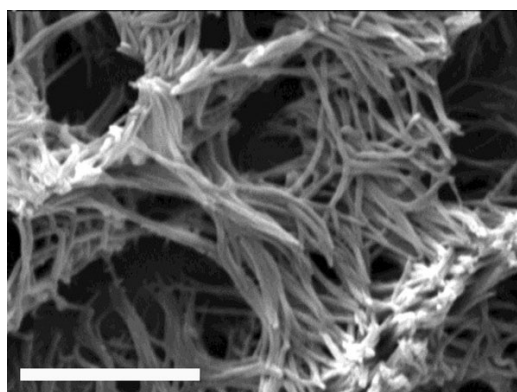
2. Materials and methods

A two-reservoir reaction chamber similar to the apparatus used by Mativetsky and Datars [22] was used to prepare the PPy(pTS) nanowire samples. A few minor modifications were necessary to accommodate a different sample fabrication method. The reaction chamber was constructed to simultaneously hold a large volume of an oxidizing solution and a much smaller volume of pyrrole monomer solution. The two solutions were separated by a nucleopore track-etch polycarbonate membrane with either a 50 or 100 nm pore size. Polymerization occurs as the pyrrole is exposed to the oxidizer within the pores of membrane, resulting in PPy(pTS) that match the pore size and the thickness of the membrane (in our case, 50 or 100 nm diameter and 6 μm length).

The polycarbonate membrane was loaded into the reaction apparatus such that the shiny side of the membrane would face the pyrrole side of the reservoirs. 70 ml of aqueous oxidizing solution containing 0.1 M iron (III) chloride plus 0.125 M of the dopant sodium p-toluenesulfonate (Na-pTS) (Aldrich 15253-6) was loaded in the larger chamber. After making sure that there were no air bubbles under the membrane, 10 ml of an aqueous monomer solution consisting of 0.3 M of twice distilled pyrrole monomer and 0.125 M Na-pTS was loaded in the smaller chamber and allowed to react for 30 min. The membrane containing PPy nanowires was then removed from the reaction apparatus and soaked overnight in deionized water. The membrane was sonicated in ethanol for 30 min to remove loosely bound PPy on the surface of the membrane, washed with deionized water, then dried overnight in an oven at 60 °C.

SEM (scanning electron microscopy) was used to image the PPy(pTS) nanostructures. Portions of the membranes containing PPy(pTS) nanowires were cut and fixed onto an SEM sample chuck using conducting carbon tape. The PPy(pTS) membrane sample was wetted in 1 ml of chloroform followed by a washing process using acetone, methanol, and

30 μm in width) of varying thickness (1–1.5 μm) of dodecylbenzenesulfonate (DBS) doped PPy, which had been grown potentiostatically on a gold surface [27]. The volume change was measured by taking height profiles of the pattern by atomic force microscopy (AFM) of the PPy(DBS) pattern at both the oxidized (0 V) and reduced (−1 V) states. The dimensional expansion reported was between 15 and 35%. Suárez and Compton showed morphology changes during the electrochemical deposition of films on various electrode surfaces [28]. They also observed the volume change behavior of a 350 nm thick PPy film doped with p-toluenesulfonate (pTS). A change of approximately 10% in height data was seen, but the behavior was very irregular under periodic voltage cycling. The paper also reports actuation limited to a single voltage cycle for PPy doped with ClO_4. This shows the importance of the dopant and the electrolyte species used for the experiments. As far as we know, all the doped PPy films used for actuation studies until now have been prepared by electrochemistry.

An alternate method of preparing conjugated polymer micro- and nanostructures is by using a membrane template, either a track-etched polymer [22] or a porous aluminum oxide membrane [10]. The polymer can be polymerized, either chemically or electrochemically, within the pore structure of the membrane, to ultimately take on the dimensions of the pore, both in length and thickness [29, 20, 21, 9, 7, 18, 11, 17]. The samples prepared by the template synthesis method have been studied for mechanical [4] and electrical properties [22, 24], for example for potential application as interconnects in computing structures [2, 1] and sensors [25]. PPy wires with diameters ∼200 nm were synthesized electrochemically on membrane pores by Berdichevsky and Lo [3], who showed qualitatively that these submicron wires changed dimensions when subjected to a redox cycle. They also obtained quantitative evidence of change of volume for a mat of such wires. Their wires were beyond the accepted 1–100 nm range for nanoobjects, and no quantitative information on the actuation behavior of single wires was reported. Absence of quantitative electrical and mechanical data makes it difficult, if not impossible, to compare the results between nano-, micro- and millimeter scale PPy. No actuation has been demonstrated prior to our work for chemically synthesized PPy micro and nanostructures, as pointed out in Smela's review [26].

Figure 2. Schematic cross-section of PPy(pTS) nanowire samples imbedded in the polycarbonate membrane as support. Also shown are the location of electrodes for the actuation and cyclic voltammetry experiment. The PPy(pTS) nanowire, AFM tip, RE and CE are all submerged in a 0.1 M aqueous solution of the dopant.

Figure 3. SEM of partially dissolved polycarbonate membrane showing the individual 50 nm diameter PPy(pTS) nanowires. (Bar = 5 μm.)

then water, in order to dissolve away a thin layer of the polycarbonate material of the membrane.

For cyclic voltammetry (CV) and AFM actuation experiments, polycarbonate membranes containing freshly prepared PPy(pTS) nanowires were further treated to electrically connect the PPy(pTS) nanowires to our experimental setup. 10 nm of chromium followed by 100 nm of gold were evaporated onto the side of the membrane that was originally dull before the pyrrole polymerization took place, to serve as the working electrode (WE) for the electrochemical actuation process. This sample was fixed onto a glass coverslip using epoxy and secured onto a sample stage by a teflon liquid sample cell. AFM (Molecular Imaging Corp. PicoSPM) was used to obtain AC mode topography images using an oxide-sharpened silicon nitride cantilever having a nominal spring constant of 0.06 N m^{-1} (Veeco NP-S). Platinum and silver wires were brought into contact with the electrolyte solution to serve as counter electrode (CE) and quasi-reference electrode (RE), respectively. A potentiostat (Molecular Imaging Corp. PicoStat) was used to perform CV measurements of the PPy(pTS)
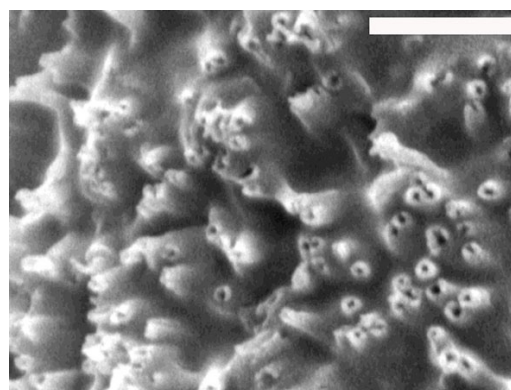
Figure 4. SEM end-view of 100 nm diameter PPy(pTS) nanowires after having the polycarbonate partially dissolved. It is thought that the nanowires that were freely protruding had broken off to reveal hollow centers. (Bar = 2 μm.)

Table 1. Reduction peak and current for each CV cycle corresponding to figure 5.

Cycle	Reduction peak (V)	Current (mA)
1	−0.746	−0.804
2	−0.697	−0.555
3	−0.697	−0.508
4	−0.697	−0.486
5	−0.696	−0.469
9	−0.686	−0.426

nanowires, as well as to control the voltage for the actuation experiments. The schematic of the setup is shown in figure 2.
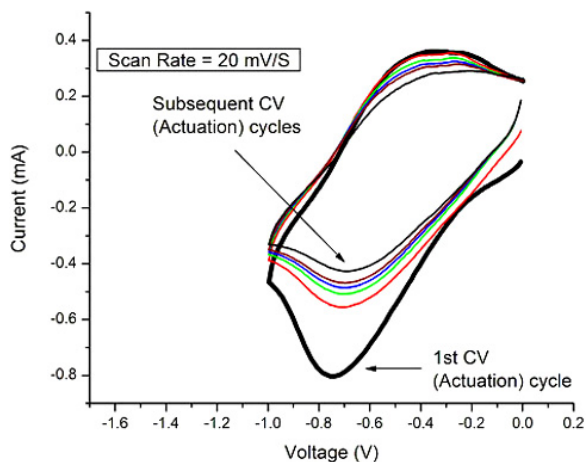
The actuation behavior of the PPy(pTS) nanowires was studied by electrochemical AFM. The equipment used for CV measurements was also used to control the oxidation state of the nanowires. AFM images were taken of the PPy(pTS) nanowire samples to compare the topography of the surface in the native oxidized state (0 V), reduced state (−1 V), and reoxidized natural state (0 V).

3. Results and discussion

The 50 nm diameter PPy(pTS) nanowires were found to be solid (figure 3). For similarly prepared 100 nm diameter nanowires, SEM micrographs revealed hollow centers (figure 4), which is in agreement with transmission electron microscope (TEM) studies of PPy(pTS) nanowires by Mativetsky and Datars [22].

The CV experiments indicated interesting differences between samples which differed only in the diameters of the isopore membranes used for their preparation. CV for the 100 nm diameter PPy(pTS) nanowire (figure 5) showed a reduction potential at about −0.7 V (table 1), as expected. However, CV for the 50 nm diameter PPy(pTS) sample (figure 6) showed a much lower reduction potential of about −1 V (table 2).

The actuation (dimension change) process for PPy(pTS) nanowires was found to be dependent on the quality of the nanowire as well as its confinement configuration.

Figure 5. CV curves corresponding to the actuation cycles for the 100 nm diameter PPy(pTS) nanowire sample. Note the difference in curves for the 1st cycle in comparison to the rest of the CV cycles.
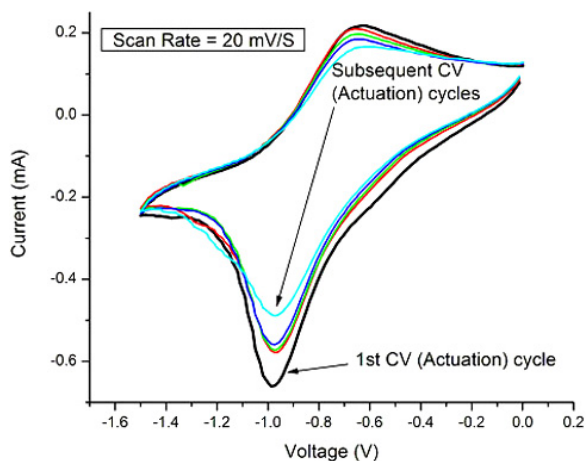

**Figure 6.** CV curves corresponding to the actuation cycles for the 50 nm diameter PPy(pTS) nanowire sample.

Table 2. Reduction peak and current for each CV cycle corresponding to figure 6.

Cycle	Reduction peak (V)	Current (mA)
1	−0.987	−0.661
2	−0.972	−0.579
3	−0.971	−0.573
4	−0.971	−0.559
5	−0.972	−0.489

Confinement configuration refers to whether any part of the nanowire is exposed from the polycarbonate membrane. Nanowires prior to the chloroform etch are fully confined and not exposed to the electrolyte solution except at the very end of the structure. It was found that having only the ends of the PPy(pTS) exposed to the electrolyte solution is not enough to observe dimension-changing behavior simply by analyzing the topography image from the AFM. A real-time actuation study was performed by placing and holding the AFM tip over what was thought to be the end of a 50 nm diameter PPy(pTS)
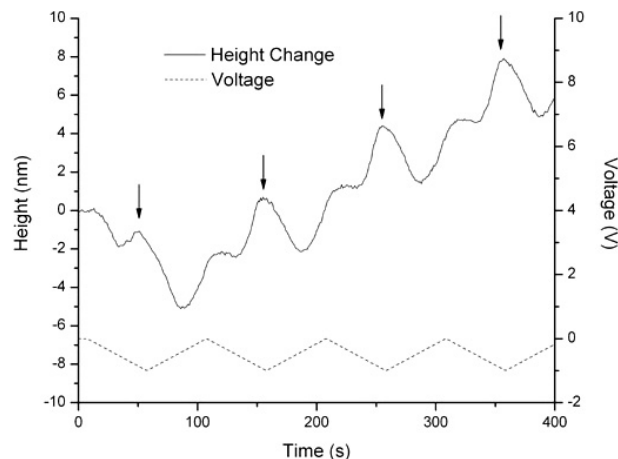
Figure 7. Real-time actuation analysis for the 50 nm diameter PPy(pTS) nanowire confined in a polycarbonate membrane as the voltage is cycled from 0 to −1 V. As expected, the nanowire shows cyclical increase and decrease behavior, with the greatest change in height at −1 V.
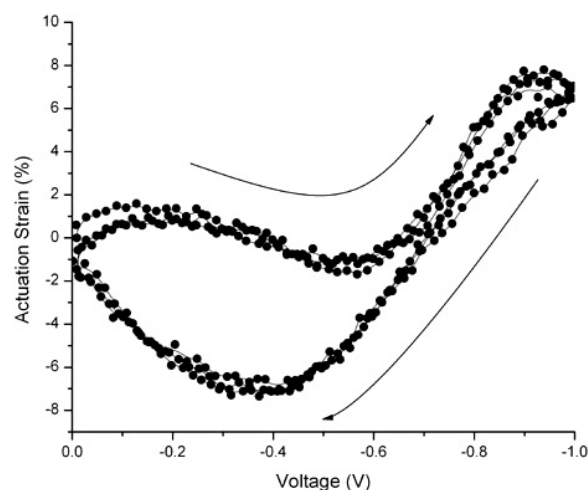

Figure 8. Actuation strain plot for the 50 nm diameter PPy(pTS) nanowire confined in a polycarbonate membrane as the voltage is cycled from 0 to −1 V. Linear actuation response can be seen from approximately −0.6 to −1.0 V.

nanowire. The result shown in figure 7 indicates that a height change of approximately 4 nm occurs in the actuation process.

The overall increase in measured height as time goes by is attributed to vertical drift of the AFM. By considering the data subsequent to the first voltage cycle (which differs from the steady-state behavior, as shown in figures 5 and 6), and correcting for the drift in height, an actuation strain curve was generated, as shown in figure 8. It should be noted that the initial height of 28 nm used in calculating the strain is not considered reliable because of measurement difficulties. However, this uncertainty affects the actuation strain in the graph only through a multiplicative scaling factor, and does not change the shape of the scatter plot. The actuation strain curve reveals hysteretic, nonlinear behavior for voltages between 0 and −0.6 V. Approximately linear behavior, which is normally preferred for actuator applications, occurs for voltages between −0.6 and −1 V.
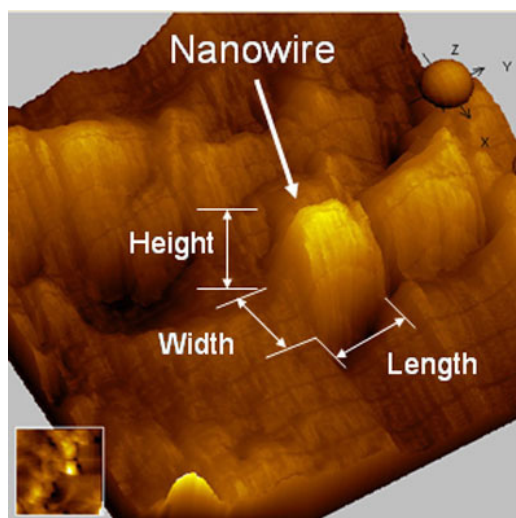
Figure 9. Three-dimensional AFM rendering showing a PPy(pTS) nanowire protruding from the surface of the polycarbonate membrane. Chloroform etch of the membrane surface was performed to expose more of the nanowires that are embedded through the thickness of the membrane.

A slight modification to the sample exposed more of the PPy(pTS) nanowires protruding from the surface. Although most of the nanowire remained imbedded in the polycarbonate membrane, a segment at the end of the nanowire was exposed due to the removal of the polycarbonate from the surface by a chloroform etch (figure 9). Subsequent electrochemical AFM experiments successfully revealed actuation of the 50 nm diameter PPy(pTS) nanowire as a function of oxidation state. Figures 10–12 show the topography of the 50 nm PPy(pTS) nanowires under different oxidation states. In all three figures, the topography images were 2nd order flattened and set to the height scale of 150 nm. Clear differences in the sizes of the nanowire structures can be seen between the different oxidation states. Although many nanowires are visible in the images, quantifying the actuation process is difficult because of the three-dimensional nature of the volume change. The effect of the AFM tip size, which typically has a radius of 5–40 nm according to the manufacturer, will distort the lateral measurements of dimensional change. Also, the orientation of the exposed nanowires further complicates quantification since longer ones seem to be lying down on the surface, while others seem to be upright. With these issues in mind, four distinct nanowire structures were chosen among many because they seemed amenable to analysis. In an effort to quantify the dimensions of the PPy(pTS) nanostructures, the height of the PPy(pTS) nanowire was measured at the highest point of the structure through cross-section analysis. The length was taken in the direction of the elongated segment of the exposed PPy(pTS) nanowire, and the width taken at the midpoint of the length. Figure 9 depicts the measurement scheme for the nanowire dimensions. Figure 13 shows the dimensional change for the each of the four nanowires cycled between different oxidation states. One can see in most cases a significant dimensional change. In the reoxidation of the sample, the dimensions do not completely return to their original values.
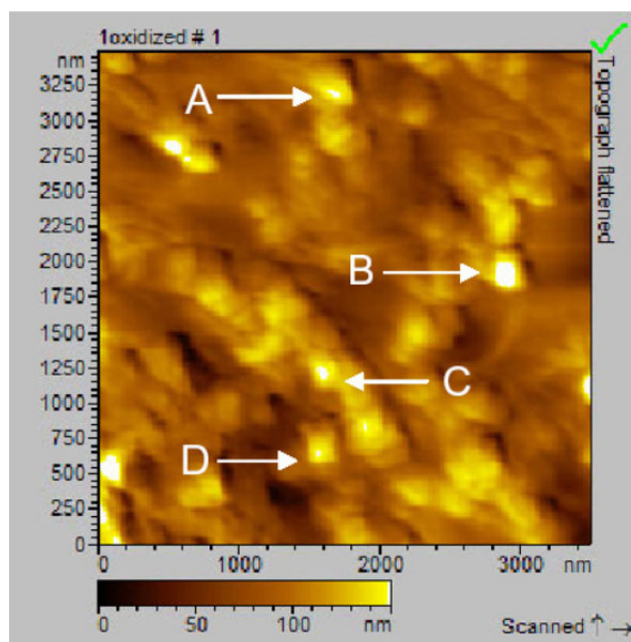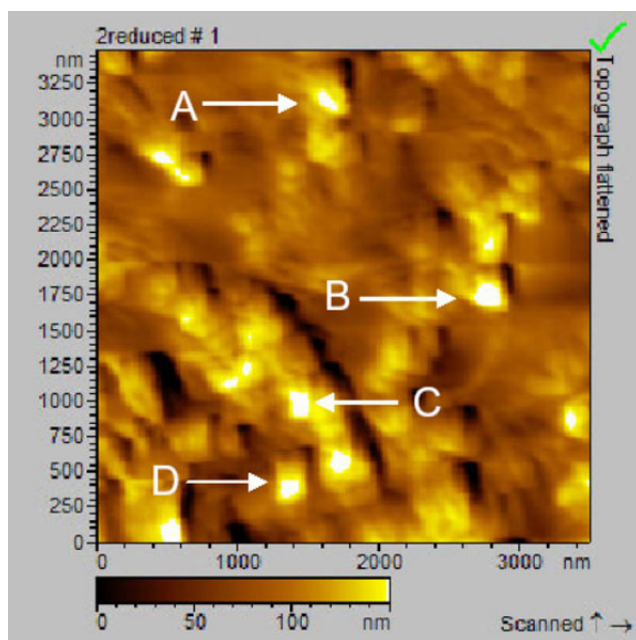

Figure 10. Initial topography image of 50 nm diameter PPy(pTS) nanowire segments protruding from the polycarbonate background. The nanowires are in the oxidized state at 0 V. Four nanowires have been chosen for analysis. The dimensions of each of the nanowires are as follows (A: height = 773.46 Å, width = 319.0 nm, length = 207.1 nm; B: height = 1130.60 Å, width = 283.4 nm, length = 200.6 nm; C: height = 615.66 Å, width = 237.3 nm, length = 164.5 nm; D: height = 790.08 Å, width = 308.4 nm, length = 197.3 nm).

Table 3. Actuation analysis of 50 nm diameter of PPy(pTS) nanowires.

Nanowire	Initial height (nm)	Height strain (%)	Initial length (nm)	Length strain (%)	Initial width (nm)	Width strain (%)
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

Table 3 shows that the actuation strain can range from 1.45% to approximately 36% at its greatest.
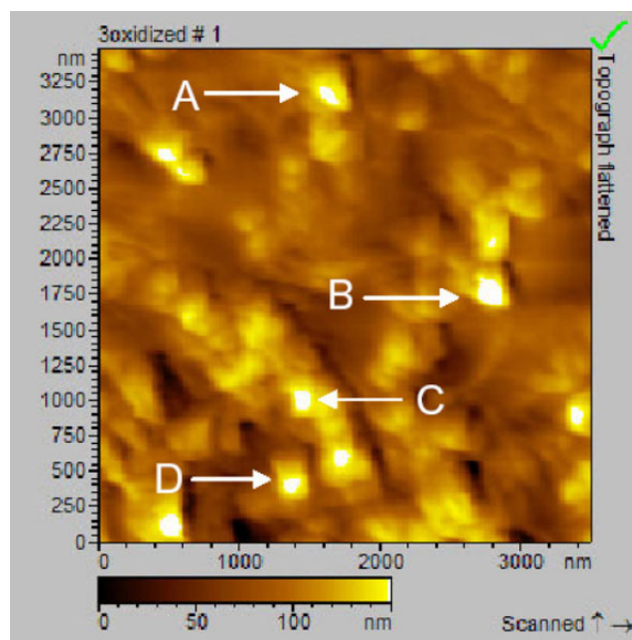
Although these PPy(pTS) nanowires have not yet been integrated into useful nanoactuator devices, the swelling and unswelling motion of the nanowires can provide the basis for such actuators. The minimum force that is exerted by the actuation of the nanowire can be estimated by using the vertical displacement of the AFM cantilever. For instance, if the value of the cantilever spring constant is taken to be its nominal value (provided by the vendor) of 60 pN nm^{-1}, the real-time actuation study shown in figure 7 shows an approximate vertical cantilever movement of about 4 nm, giving a force of about 240 pN. In the case of the 50 nm diameter nanowire 'C' in figure 13, a vertical change of about 22 nm (or 36% strain) was observed. Although the polymer in this experiment was not working against a cantilever, if we extrapolate the earlier results to this case we find a corresponding actuation force of ∼1.32 nN.
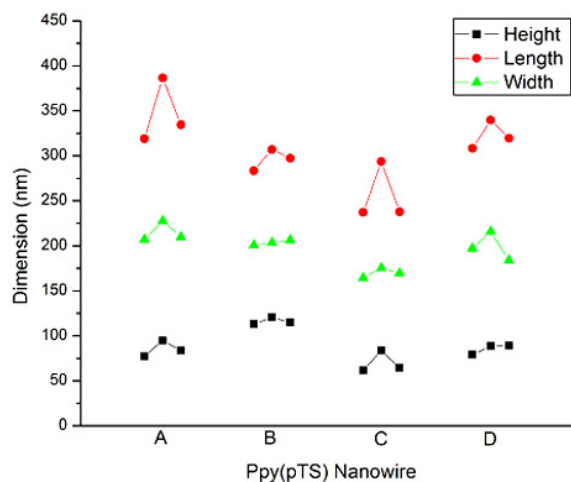
Figure 11. Topography image of 50 nm diameter PPy(pTS) nanowire segments protruding from the polycarbonate background. The nanowires are in the reduced state (actuated) at −1 V. Four nanowires have been chosen for analysis. The dimensions of each of the nanowires are as follows (A: height = 946.85 Å, width = 386.5 nm, length = 227.5 nm; B: height = 1206.40 Å, width = 307.0 nm, length = 203.5 nm; C: height = 838.87 Å, width = 293.8 nm, length = 175.4 nm; D: height = 886.90 Å, width = 339.7 nm, length = 215.9 nm).

Figure 12. Topography image of 50 nm diameter PPy(pTS) nanowire segments protruding from the polycarbonate background. The nanowires are back in the oxidized state at 0 V after having been actuated. Four nanowires have been chosen for analysis. The dimensions of each of the nanowires are as follows (A: height = 836.79 Å, width = 334.6 nm, length = 209.8 nm; B: height = 1148.26 Å, width = 297.2 nm, length = 206.3 nm; C: height = 643.69 Å, width = 237.6 nm, length = 169.5 nm; D: height = 889.74 Å, width = 319.6 nm, length = 183.9 nm).

Several issues need to be addressed before nanoactuators based on electroactive polymers can find device applications. Our actuation experiments have shown that the volume change process at the nanoscale is not very consistent. This may be due to many reasons, such as lack of uniformity in the dopant concentration and local variation in the polymer structure itself, which other researchers have found is dependent on the fabrication procedure. Because of the many factors that affect the quality and the various properties of the PPy, volume change percentages and properties cannot be compared directly across experiments, as pointed out in the literature [6, 26, 27].

A methodology for establishing performance metrics for these nanoscale actuators is presently unavailable. For bulk samples, measurements have been made which suggest values in the range of ∼1% dimensional change with an actuation stress of ∼3 MPa for a linear actuator [6] and 0.22 N for a bimorph structure [19]. Research reports of this type are sparse. An estimate was made above for the minimum actuation force observed by the cantilever, but this estimate is coarse. Measuring the true actuation force for these nanowires is a challenge, primarily because of the difficulty in repeating the same experiment to ultimately find the balance point of the actuation and mechanical resistance from the cantilever. AFM-based methods seem promising, and, in addition to the estimates made here, the AFM has already been employed for measuring the elastic modulus [4] as well as the electrical resistivity [24] for nanoscale PPy fibers in the dry state. There are many additional issues that make the task of measuring

Figure 13. Analysis of each of the individual 50 nm diameter PPy(pTS) nanowires (A–D). The three points in each data set correspond to the initial oxidized state, reduction, then reoxidation of the nanowires.

the actuation force challenging. For example, it is known that the elastic modulus can change drastically between different oxidation states, and the dimensional-change behavior has been shown to be complex (figures 10–12).

There are clear benefits to miniaturization for potential PPy-based devices. For example, the time required for switching between oxidation states is vastly improved from

~5 s for bulk millimeter scale material. Calculations have not been performed for switching speeds of nanoscale PPy, but our CV data for the PPy(pTS) nanowires with 50 nm diameter show sharp reduction peaks (figure 6), indicating that most of the pyrrole rings change oxidation states together. In contrast, a broader peak is observed for the larger 100 nm diameter PPy(pTS) nanowires (figure 5), indicating a slower process of change of oxidation state. If the trend follows the results of Lewis and co-workers, the actuation force may also be enhanced if smaller and/or thinner PPy structures are used [19].

The 50 nm diameter PPy(pTS) nanowires seem to be very compliant. This will limit their applicability in devices. Cuenot and co-workers measured the elastic modulus to be ~1.2 to ~3.2 GPa for ~100 nm diameter PPy nanowires (electrochemically polymerized), which falls within the range of values for bulk PPy [5]. In the same research, however, a much higher elastic modulus of 60 GPa was observed for 35 nm diameter PPy nanowires (measured in a dry state). Since our 50 nm diameter PPy(pTS) nanowires fall between the range of 35 and 100 nm, the value of their elastic modulus is not clear.

In conclusion, nanoscale actuation for individual polypyrrole-based nanowires has been quantitatively demonstrated for the first time. It was found that only regions of the nanowires exposed to the aqueous solution are active for swelling. Quantification of actuation properties is difficult because of the small scale as well as the geometry of actuated PPy(pTS). CV experiments suggest that the 50 nm diameter nanowires are more ordered than their 100 nm counterparts. This trend is supported by other research works [16]. We have made an estimate for the minimum actuation force that is observed, but more robust methodology needs to be developed to further the design and application of the nanowires in the future.

Acknowledgments

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