

Modified Polypyrrole Nanowire Networks for Electrochemical Sensors

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Abstract

Polypyrrole (PPy) nanowires grown via template synthesis are ionically imprinted in order to create a selective material for aqueous sensor applications. PPy nanowires grown in the presence of nitrates exhibit changes in potentiometric and galvanometric response with respect to ionic constituents of solutions in contact. Nanowire networks isolated on indium tin oxide (ITO) substrates are examined using 2 point conductivity measurements and impedance spectroscopy under various electrolyte species and solution concentrations in order to investigate possible detection limits, selectivities and sensitivities as hypothetical materials for new ion-selective electrodes, specifically for nitrate detection.

Keywords: nanowires, polypyrrole, anion, chemical sensors, electrolyte, conductivity

Introduction

Innovations in sensor technology have resulted in smaller and more sensitive chemical and biological detection than previously available [1-4]. The incorporation of nanomaterials (such as carbon nanotubes [5-7], silicon dioxide nanosprings [8], and gallium nitride nanowires [9]) into sensor platforms is showing promise of increasing detection limits for a variety of chemical and biological applications. Due to the high surface to volume ratio of nanostructures, nano-based sensors are further evolving in order to exploit the higher affinity interactions between nanomaterials and species of interest. Molecular imprinting of nanostructures is finding its way into popular avenues of research as new combinations of nanomaterial and imprinted molecules or dopants are explored to take further advantage of the nanoscale interactions present with these developments [10-12]. Nano-based sensors are targeted to exploit surface sensitivity to increase affinities for binding events or chemical interactions for more efficient approaches to detection, characterization, and monitoring needs.

Although numerous varieties of materials can be used to produce nanostructures, polypyrrole nanowires is an attractive polymer due to its conducting nature and versatility during synthesis [13-15]. Two predominant methods of synthesizing polypyrrole have been reported: electrochemical synthesis [16] and template synthesis [17]. Electrochemical synthesis can be an attractive means of synthesizing nanostructures, offering a wide range of physical properties, such as length and diameter. However, this requires more stringent control during production than the simpler template synthesis method.

Uniform nanowires can be produced using a minimum of chemical reagents and simple experimental apparatuses. Nanowire dimensions can easily be controlled using porous membranes of a particular diameter; a large variety of imprinting molecules can easily be incorporated from solution into the nanostructure in order to confer ionic selectivity towards an anionic sensor material.

Methods and Materials

Polypyrrole Nanowire Synthesis. Nitrate imprinted polypyrrole nanowires are produced via template synthesis using 0.1 μm diameter Isopore[®] polycarbonate membranes (Millipore). The membrane is held in place using a Teflon[®] ring, creating a fluid barrier between the interior and exterior of the reaction vessel. Pyrrole (Sigma-Aldrich) is used as provided and diluted to 0.2 M concentrations with 0.13 mL pyrrole in 10 mL dionized-H₂O (di-H₂O). A 0.2 M oxidizing solution is made using 3.8 g *p*-toluenesulfonic acid (*p*-TSA, Sigma-Aldrich), 3.24 g ferric chloride (FeCl₃, Sigma-Aldrich) and 1.7 g sodium nitrate (NaNO₃, Sigma-Aldrich). NaNO₃ is not included for nanowire control groups and synthesized similarly to nitrate-grown samples. The pyrrole solution is placed within the reaction vessel and submerged in oxidizing solution for one hour at 5 °C.

After polymerization, the reaction is halted by rinsing the membrane with di-H₂O and polished lightly using an ultrafine grit alumina sandpaper to remove any buildup of polypyrrole on the surface of the membrane. The membrane is dissolved with methylene chloride and sonicated in tetrahydrofuran

(THF) for 1 to 2 hours, or until the nanowires are completely dispersed.

THF is removed from the nanowires by vacuum filtration using 0.1 μm diameter alumina Anodisc® membranes (Whatman) and rinsed using ethanol followed by di- H_2O . Filtered nanowires are suspended in 10 mL di- H_2O to maintain a consistent density of nanowires in solution. Centrifuging the sample and decanting the nitrate rich water removes the remaining nitrate within the nanowires. Ten mL fresh di- H_2O is added and the nitrate removal process is repeated until nitrate levels are below detectable colorimetric limits.

Polypyrrole Nanowire Morphology. Dispersed PPy nanowires are cylindrical wires with an average diameter of 150 nm and lengths varying between 2 and 3 μm . An average individual nanowire is shown in Figure 1. Nanowire lengths can be adjusted with longer polishing times resulting in shorter nanowires. With a lesser amount of polishing and shorter sonication times, greater amounts of nanowires remain connected to each other at either end. Figure 2 shows a nanowire “bundle” which is used homogeneously with fully dispersed nanowires.

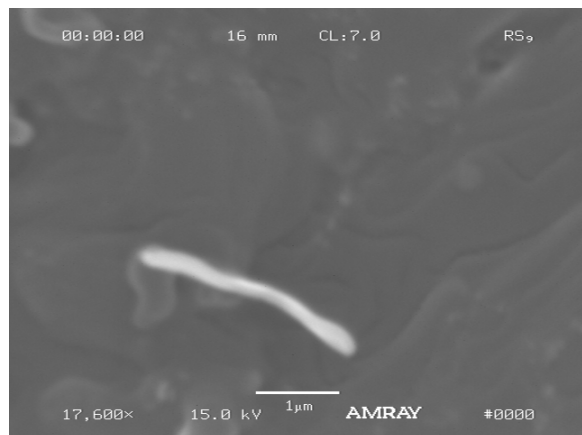


Figure 1. SEM of an individual PPy nanowire.

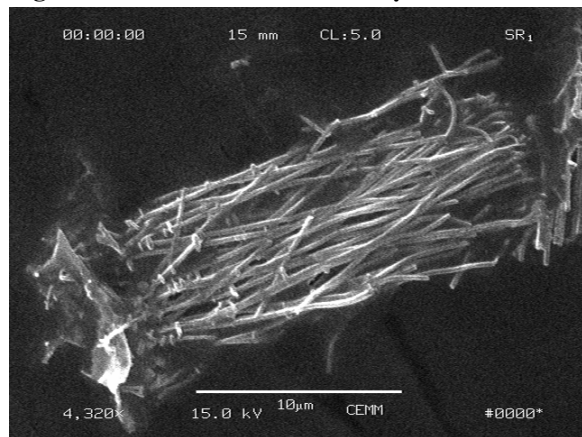


Figure 2. FESEM of a PPy nanowire “bundle”. Left end of the bundle shows the attachment of nanowires to each other.

Nanowire mats are deposited dropwise onto an indium tin oxide (ITO) plate (Delta Technologies) as shown in Figure 3.

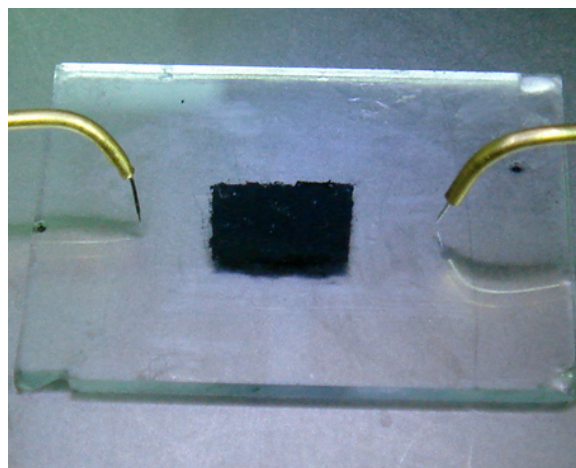


Figure 3. PPy nanowire mat on ITO plate. The clear strip through the middle is the non-conducting line, which forces the current through the network of PPy nanowires.

Prior to deposition, a non-conducting gap is etched into the ITO plate using an acidic etching solution to create a gap 3 mm between the two sides of the ITO plate. The nanowire mat is deposited using a tape mask to produce a nanowire mat of approximately 25 mm². A typical nanowire mat is shown in Figure 4 and shows the random network of individual and bundled PPy nanowires.

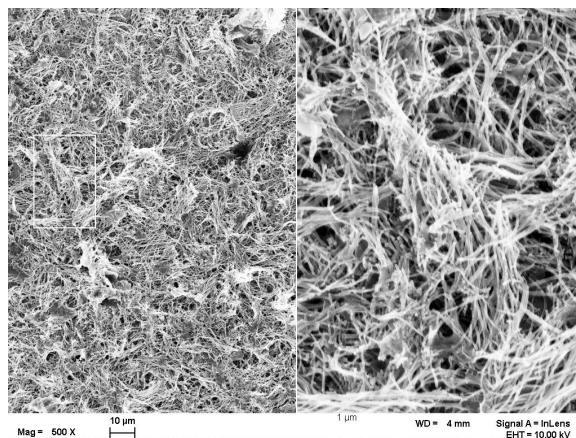


Figure 4. FESEM of PPy nanowire mat as tested. Right SEM image is highlighting a nanowire bundle in the mat.

These mats have an average thickness of 10 μm , shown in Figure 5, and allow a significant path for conduction through the network. The use of PPy

nanowires in a matted network allows for more interaction between the surface of the individual nanowires and the electrolytic solution than would be possible in smaller, individual nanowire systems. It also provides more open volume through the mat system rather than accessing the more difficult pore volume.

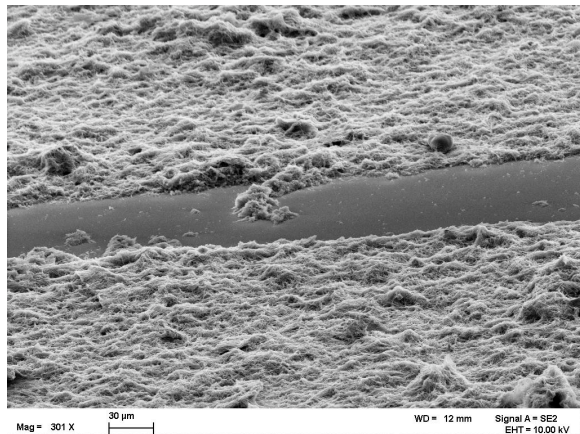


Figure 5. FESEM of PPY nanowire mat with a scratch through the mat to illustrate the average thickness of the mat as tested.

Nanowire Electrical Testing. PPY nanowire conductivity measurements are performed using a Keithley Model 4200-SCS Semiconductor Characterization System. Four samples were made for conductivity measurements. Two samples, samples 2.1 and 2.2, were synthesized in the presence of nitrates, while samples 2.3 and 2.4 were synthesized without nitrates for a control group.

Two point conductivity measurements are conducted by varying the current between 0 and 10 nA and measuring the voltage across the nanowire mat. Identical ITO plates were used for each sample of PPY nanowires. Each sample was deposited equally onto plates and allowed to dry. Each dry sample was tested for baseline conductivity data and followed by the addition of a drop of ionic solution. One plate was tested using a 5 mM sodium nitrate (NaNO_3) solution, while the other plate was tested using a 5 mM sodium chloride (NaCl) solution.

Results

Due to sensitivity in the instrumentation and the low currents used experimentally, measured voltages had a significant deviation between different samples, with deviations of up to 20% of the average measured voltages between runs. These variances are likely due to differences in the mat network of each sample. Measured voltages within each experimental run for a particular sample were much more consistent, with standard deviations of $\sim 5\%$ in voltages within each run. To compensate for this experimental noise, 20 voltage measurements were taken during each experimental run, and 10 runs performed on each sample. Arithmetic averages were taken of the data for each sample and used to examine the changes in measured voltages. Average results are tabulated in Table 1. A graphical example of the voltage shifts is shown in Figure 6 for one of the nanowire mats (sample 2.2).

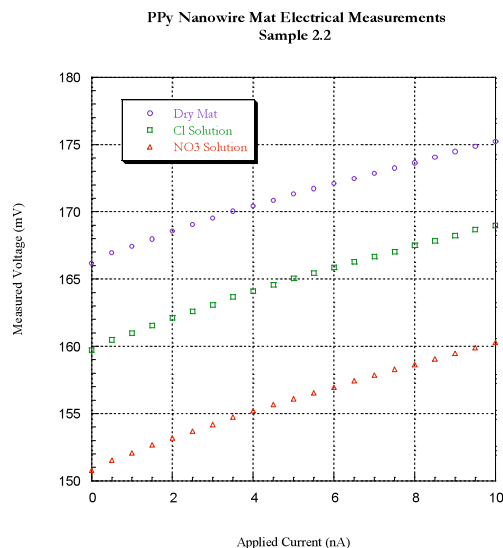


Figure 6. Average results of electrical testing on NO_3^- imprinted PPY nanowires. The results show an increase in ΔV for the nanowire mat in the 5 mM nitrate electrolyte solution.

Table 1
Average Voltage Shifts in Polypyrrole Nanowire Mat Conductivity Measurements.

Sample	Imprinting	Average Voltage Shift (mV)		
		NO_3	Cl (Control)	Ratio
2.1	Nitrate	40.4	21.8	1.85
2.2	Nitrate	15.2	6.3	2.40
2.3	None (Control)	19.9	53.7	0.37
2.4	None (Control)	28.6	71.9	0.40

This demonstrates that the potential shift from the dry “baseline” mat is much greater for the nitrate solution when the PPy nanowire has been imprinted with nitrates during synthesis.

Determining the conductivity of the system under the various electrolyte solutions for the different nanowire samples shows the applicability of PPy nanowires towards an anionic sensor platform. Conductivity results for four samples are shown in Table 2, and show an inherent difference between these imprinted and non-imprinted nanowire samples.

As expected, the conductivity for each sample increased with the addition of either ionic solution since electrons are free to flow through the aqueous network versus being restricted to traveling only through the dry nanowire network. With nitrate-imprinted nanowires, the increase in conductivity for the nitrate solution tests was 6 to 6.7 $\mu\text{S}/\text{m}$ greater than the increase for chloride solution tests. With the control group of non-imprinted wires, the increase in conductivity was 2.2 to 3.8 $\mu\text{S}/\text{m}$ greater for the chloride solution tests than the increases found in nitrate solutions. The increase for non-imprinted samples is attributable to the greater electronegativity of the chloride ion and the greater inherent conductivity of a chloride solution relative to an equimolar solution of sodium nitrate.

The difference seen in nitrate-imprinted nanowires may be attributable to surface charge changes caused by adsorption and desorption of ionic species on the outer surface of the nanowires [18,19]. Ionic permeation into the nanowire cannot be ruled out though, and a better understanding of this complex behavior is needed before explanations are made.

Current Work. Better understanding of the mechanism responsible for these conductivity results seen will require an accurate model capable of separating the capacitive nature of the nanowire network from its resistive nature. In order to understand these differences, impedance spectroscopy is being utilized to examine the complex and real differences in impedance through the system, as well as building an accurate model through the design of an equivalent circuit. With an accurate model, quantification of the electrical response of imprinted PPy nanowires will be more readily accomplished, and the mechanism responsible for these early results seen under various electrolytic solutions can be better understood.

Conclusions

These results show the success of imprinting polypyrrole with an ionic species and the promise of the imprinted polymer as a means for detection of a target analyte species in solution. Incorporation into a sensor will utilize these unique electrical differences to identify species of interest and lead to quantification of species present in the sensor environment. Future work will involve the imprinting of other ionic species to establish a general method for anionic sensors fabrication based upon imprinted polypyrrole nanowires.

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Table 2
Change in conductivity for PPy nanowire mat ($\Delta\sigma$ [=] $\mu\text{Siemens}/\text{m}$)

Sample Solution	2.1		2.2		2.3		2.4	
	NO_3^-	Cl^-	NO_3^-	Cl^-	NO_3^-	Cl^-	NO_3^-	Cl^-
$\Delta\sigma$	3.00	2.40	1.11	0.44	2.22	4.42	2.00	5.84

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