The Pennsylvania State University
The Graduate School
Department of Chemistry

SYNTHESIS AND INTEGRATION OF CONJUGATED POLYMER
NANOSTRUCTURES FOR SENSING AND OTHER APPLICATIONS

A Dissertation in
Chemistry
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2008
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ABSTRACT

Miscellaneous conducting polymer nanostructures have been investigated for their potential applications in sensors, energy storage devices and artificial motors. One-dimensional nanowires and nanotubes were synthesized chemically or electrochemically using a hard template replication technique. Their morphology can be controlled to some extent by tuning the synthetic conditions. Core-shell spheres with silica cores and conducting polymer shells have been fabricated. The electrical properties of individual nanoparticles were investigated and harnessed for chemical sensing. Their electrochemical properties were explored for energy storage applications.

These nanoparticles have been investigated as building blocks towards next-generation electronic devices. High-density arrays have been demonstrated through electric field-directed assembly or capillary force-assisted assembly of these nanostructures.

Composite nanowires with conducting polymer and magnetite nanocrystals have also been investigated. Materials embedded in the nanowires can bring additional functionalities into the conducting polymer system. This was exemplified by the development of an artificial motor with appropriate magnetic and catalytic properties which successfully achieved autonomous movement on designated pathways.
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ACKNOWLEDGEMENTS

Without my research advisor, Professor Thomas E. Mallouk, this thesis could never have been possible. I would like to thank him for this precious learning experience in his group, for giving me support, trust and advises whenever I needed. He helped me to grow into a scientist and taught the importance of taking an overall perspective in research, from which I will benefit for the rest of my life.

I consider myself lucky to have Professor Theresa S. Mayer as a collaborator, mentor and committee member. From wafer fabrication to manuscript revising, from crucial technical suggestions to caring for my career, she has been wonderful in every aspect. I also thank the rest of my thesis committee: Dr. Ayusman Sen and Dr. Christine Dolan Keating for their continuous support for five years to my work at Penn State.

Many people in Professor Mayer’s group contributed to this thesis work. Jaekyun Kim did most of the semiconductor fabrication. In the last three years, he has always taken my requests as his priority, which I appreciate from the bottom of my heart. An excellent experimental physicist, Dr. Alexey E. Kovalev, has been on the journey to explore the transport and noise of conducting polymer nanowires with me from the very beginning. I would like to thank him for sacrificing a lot of his weekend and night time to work with me. Richard T. Geiger set up the gas supply system for the sensing measurements. Many other members of this group also generously devoted some of their time to help me around their lab.

The Mallouk group is a unique group of people I would like to acknowledge too. This is a group with diversified projects. But one thing is common - everyone has a good
heart. They wanted good things for others. They are always there to help. The friendship I have developed with some group members will extend way into the future.

My friends have lightened my life. They are my source of energy. Special thanks to Rose Hernandez, for teaching me English, leading me into the western culture and for being the one I can always go to for spiritual support.

My last acknowledgement goes to my husband, Xianfeng Sun. He has created the most challenging project for me to work on – human relationship. Without him, I could have finished my PhD studies a year earlier. But life would have been less meaningful.

This thesis is dedicated to my family in the name of love.
Chapter 1

Introduction

1.1 Nanoscale Science and Technology

The field of nanoscience and nanotechnology has been growing at an astonishing speed in the last two decades. Figure 1-1 shows the number of publications containing the keyword “nano” included by SciFinder Scholar in each calendar year since 1988.\textsuperscript{1} Despite some initial disproportionately high excitement, research in this area has indeed made some positive impact on science and technology.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The number of publications containing the keyword “nano” included by SciFinder Scholar in each calendar year over the past two decades.}
\end{figure}
The drive behind this fast growth is the demonstrated and potential advantages “nano” has to offer. Quantum confinement brings new properties unseen in bulk materials to semiconductor nanocrystals. High surface-to-volume ratio can improve catalyst and sensor performance. Another feature of “nano” is the possibility to achieve high density packing, which is best exemplified in electronics. The growth of the semiconductor industry essentially depends on the miniaturizing of transistors or, in a broader sense, the fine control of materials at the nanometer scale.

1.2 Building Materials and Devices from the Bottom Up

An important theme in nanoscience and technology is the assembly of “building blocks”. This “bottom-up” approach opens up possibilities to tremendous new materials and devices. The Mallouk group at Penn State University has been exploring a broad range of building blocks and using the assembly strategy to seek solutions to miscellaneous problems related to energy, environment, electronics and so on. In terms of building blocks with interesting electronic properties, a library of nanowires based on metals, semiconductors, oxides, molecular junctions and conducting polymers have been developed.

Over the years, this group and many other groups around the world have accumulated a certain degree of understanding of the basic assembly rules of nanoscale and microscale objects. Chemical bonding, physical bonding between the substrate and building blocks or interactions between building blocks can be utilized to achieve “self-assembly”. Outside forces induced by the electrical field, magnetic field or light
have been harnessed to achieve precise manipulation of certain objects. But this field is far from reaching its full potential. The close collaboration between science and engineering is about to bring complex integrated systems from concepts to reality.  

1.3 Organization

The stories in this thesis are set in the overall perspective described above. The objectives of this thesis are: 1) to use conducting polymer nanostructures as a model system to answer some of the fundamental questions related to their synthetic control, integration and electrical transport properties; 2) to document the exploratory research on the potential of conducting polymer nanowires, nanotubes and core-shell spheres in chemical sensors, electrochemical capacitors and artificial motors.

Chapter 2 presents an overview of the integration approach to construct high density chemical sensor arrays from nanoparticle building blocks containing conducting polymers as the active functional material. The synthesis of one-dimensional and core-shell nanostructures is the focus of this chapter. Electric field and capillary forces are used for the assembly of these nanostructures. Recent results in CMOS integration made in the Mayer group at the Electrical Engineering Department at Penn State are also mentioned. This chapter is progress summary of an exciting multidisciplinary project.

Chapter 3 discusses the electrical transport mechanism and noise characteristics of individual poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires. There appear to be connections between electrical transport properties and vapor sensing performance of these nanowires. This chapter takes the understanding of the problem to a deeper level.
The current interest of the conducting polymer electrical devices community in “nanostructure” geometry is a necessary first stage but rather superficial. Control of the electrical transport at the molecular level inside these nanostructures is the critical to the success of these devices. In collaboration with Kovalev in Mayer group, the noise characteristics of PEDOT nanowires are under current investigation. Data collected so far will be discussed.

Chapter 4 investigates the electrochemical growth of polyaniline (PANI) nanowires in anodic aluminum oxide (AAO) membranes. The influence of synthetic conditions on PANI nanowire morphology was studied. Possible mechanisms based on PANI nucleation and growth are proposed. The electrochemical capacitance of PANI nanowire arrays in AAO membranes was investigated. Nanowire array configuration, open morphology and better sample integrity were found to be beneficial to the performance of PANI in electrochemical capacitors.

Chapter 5 deals with a problem in the new field of autonomously powered artificial motors. In order to achieve guided motion of nano- or microscale objects, heterogeneous magnetic fields were designed as the movement paths. New synthetic strategies led to motors based on conducting polymer composite materials. Understanding was gained on the requirements of guided movements from the comparison of conducting polymer composite motors with a few other natural and artificial motors. The movements in the heterogeneous field were measured in Fischer’s group at Florida State University.
1.4 References and Notes

1. Data collected from the SciFinder Scholar program in March 2008.


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2.1 Introduction

Miniaturization of materials with interesting electrical properties was first driven by the needs of the electronics industry. With the traditional “top-down” fabrication in semiconductor industry approaching its economic feasibility limit, substantial work has been devoted to alternative “bottom-up” solutions. Nanoscale device elements are being explored. Methods to manipulate and assemble them into dense arrays are being developed. Schemes for addressing elements within arrays at the nanoscale are being pursued.

The influence of research on miniaturization and integration goes beyond computing. Another area that will most probably benefit is sensing. “Small and numerous” is the strategy selected by nature for most biological sensory systems during its evolution. For example, an average person has approximately 12 million human olfactory receptor cells, which contain about 500 types of odorant receptors. Redundancy plays an important role in this sophisticated sensory system. Inspired by this, optical gas sensors have been developed, which are essentially high density nano- or microscale bead arrays. Signal-to-noise ratio has been shown to increase proportionally with $n^{1/2}$, where $n$ is the number of sensor elements in the array.
Electrical sensor arrays based on the same concept presents great opportunities. Macroscopic electrical sensors, including metal oxide sensors,\textsuperscript{9} conducting polymer sensors,\textsuperscript{10} percolation-based composite sensors\textsuperscript{11} are workhorses in the sensor field nowadays. However, the task to fabricate high density arrays of them brings the following challenges:

1. Synthesis. The ability to finely confine materials’ geometry in order to achieve one, two or three dimensions of them in the nanometer range is the first barrier to overcome. Some unique problems arise in nanoparticle synthesis, which will be addressed throughout this thesis. In addition to that, each individual nanoscale sensor element has to be better or at least similar to a traditional macroscopic sensor for the final array to be really beneficial. How to achieve this or whether material properties scale with the dimensionality is still an open question.

2. Integration. For an optical sensor array described above, it is possible to address each sensing element with a CCD camera and an image analysis program.\textsuperscript{12} However, in an electrical system, this requires more complex integration systems to multiplex and read out signals from individual nanoparticles and programs with designed architecture to interface with the electronics and process the signals.

These are the problems we are working on as a multidisciplinary team with expertise in the following areas: Chemistry (Mallouk group), integration (Mayer group) and signal processing (Narayanan and Bell groups). A broad range of materials can be
incorporated into our system. We started with conducting polymers. But the integration methodology should be applicable to many other materials as well.

Since the discovery in 1977 that the conductivity of the prototype conducting polymer, polyacetylene, can increase up to seven orders of magnitude upon exposure to halogen vapor, the conjugated polymer family has been the research subject of hundreds of groups. Figure 2-1 shows some of the common conjugated polymers. They all have a conjugated backbone, i.e. alternating single and double bonds. Pristine (undoped) conjugated polymers have a filled $\pi$ band and an empty $\pi^*$ band. The energy between the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals is the $\pi-\pi^*$ energy gap, $E_g$. Since there are no partially filled bands, they are typically semiconductors. However, upon oxidation ($p$-doping) or reduction ($n$-doping), charge carriers such as solitons, polarons and bipolarons appear, creating intergap energy states. The attraction of an electron in one repeat unit to the positive charge in the neighboring units leads to carrier delocalization along and polymer chain and sometimes interchain electron transfer. Thus the polymer becomes more conducting. Disorder limits the carrier mobility and has been one of the biggest problems in this field to solve. A recent breakthrough is the true metallic transport achieved in polyaniline (PANI) through a clever control of the synthesis.

The unique combination of interesting optical, electrical and electrochemical properties and the mechanical, processing and cost advantages makes them useful in many devices. Organic light emitting diodes, electrochromic windows, antistatic coatings, electromagnetic shieldings and sensors based partially on conducting polymers have been commercialized. Solar cells and microelectronics with conducting polymer
components are being actively studied. Hernandez’s work in Mallouk group on polypyrrole (PPy)-protein composite nanowires for potential biosensing applications\textsuperscript{17} inspired and laid the foundation for our work.

The common configurations of conducting polymer-based gas sensors include: chemoresistors (resistance changes), diodes or transistors (work function changes), optical waveguides (absorption changes), quartz crystal microbalance/surface acoustic wave sensors (mass changes) fluorescence sensors (fluorescence changes) and amperometric sensors (current changes) etc.\textsuperscript{10,18} Among them, the easiest to incorporate into our system is the chemoresistor configuration.

Initially conducting polymer chemoresistor sensors were applied to the detection of electron-acceptor gases such as NO\textsubscript{2} and SO\textsubscript{2} and electron-donor gases like NH\textsubscript{3}.\textsuperscript{19}
Later, it was found that they also respond to volatile organic compounds (VOC).\textsuperscript{20-22} At low gas concentrations, the resistance change is usually reversible. Unmodified conducting polymers tend to show little specificity. But when used in “cross-reactive” sensor arrays, they can overcome this problem. Another strategy, which originated from Swager’s group and adopted by many other groups later, uses synthetic receptors or functional groups to improve conducting polymers specificity and sensitivity as well.\textsuperscript{18}

The mechanism of chemoresistor sensors based on conducting polymers is complex. First, contact resistance contributes to the overall resistance and needs to be taken into account for data interpretation. Second, several mechanisms have been proposed to explain the resistivity change from the conducting polymer itself.\textsuperscript{23-25} But sensing data seem to vary from one research lab to another depending strongly on the sample preparation and measurement conditions. The functional relationship between resistance and the concentration of the analyte gas is always empirical.\textsuperscript{26} However, one can view the resistivity change in a qualitative way as a result of the charge carrier numbers and/or mobility changes induced by the interaction between the analyte and the polymer chains and/or the counterions. More electrical transport mechanisms and gas interactions will be discussed in Chapter 3.

Chapter 2 and 3 of this thesis describe our research effort along the line of miniaturization and integration of conducting polymer sensors. Chapter 2 is focused on how to achieve dimensionality control of functional materials and the research progress on integration. Chapter 3 discusses a recent finding that the charge transport mechanism is important to the sensing performance of individual sensors. To consider resistivity change from a transport mechanism perspective is new in this field. The experimental
results provide some possible guidelines on how to achieve better sensor elements for high density arrays in the future.

2.2 One-Dimensional Nanoparticles

2.2.1 Synthesis and Characterization

In general, the fabrication techniques for conducting polymer one-dimensional nanostructures can be classified into three categories: template-free methods, soft template methods and hard template methods. Template-free methods include many creative ways to generate conducting polymer nanowires or nanotubes. For example, dip-pen nanolithography, molecular combing, electrospinning. Huang et al. developed “rapid-mixing” and “interfacial polymerization” methods to synthesize PANI nanowires chemically. Liu and coworkers developed a “three step” route to make PANI nanowires electrochemically. The most common soft templates are micelles or reversed micelles formed by surfactants. The formation of PPy nanotubes, poly(3,4-ethylenedioxythiphene) (PEDOT) nanowires with this method has been demonstrated. Liquid-crystalline phases, single DNA molecules or polyelectrolyte molecules have also been used as soft templates for the growth of conducting polymer nanowires. However, the one-dimensional nanostructures fabricated with templateless and soft template methods are usually either interconnected or non-uniform. So they are not suitable for making building blocks to construct microelectronic or nanoelectronic devices which require fine control with more precision.
Hard template methods use nanochannels as reactors for polymerization. A new branch in hard template methodology is worth noting. In the last few years, lithographically defined channels have been introduced as new templates for making one-dimensional conducting polymer nanostructures. The Myung group used electron-beam lithography to create open trenches in SiO$_2$ between microelectrodes.$^{39-41}$ Peng et al. developed a method to grow conducting polymer nanoribbons in enclosed nanochannels.$^{42}$ Tseng and Heath et al. combined the “three step” nanowire generating method with microelectrode junctions defined by lithography to make electrical junctions composed of conducting polymer nanowires.$^{43}$ The methodology represented by these three techniques is based on growing a polymer electrochemically to bridge the gap between two electrodes. It has some advantages. For example, it was shown that the built-in contacts can be ohmic in nature.$^{42}$ It is compatible with complementary metal oxide semiconductor (CMOS) fabrication technologies. Although promising, there are issues such as high cost and the poor reproducibility from wire to wire. Another clever idea originated from Chi’s group.$^{44}$ They used nanoimprint lithography (NIL) to define photoresist trenches on silicon wafers. Conducting polymers were then grown chemically. After a liftoff process, the photoresist was removed, leaving only polymer nanowires on the substrate. In order to increase the adhesion of the polymer to the silicon wafer, some pyrrole silane was mixed in with the monomer and covalently bonded in the polymer chains during polymerization. This method is easy to scale up and the polymer patterns obtained can be uniform. However, there are potential contact problems involved. Also the mixed-in pyrrole silane could have a deleterious effect on the electrical properties of the nanowires.
Conventional hard templates include AAO membranes and track-etched polycarbonate membranes. The deposition inside the pores can be achieved through chemical/electrochemical polymerization in solution. Vapor deposition has also been shown as an effective way to fabricate one-dimensional nanostructures inside membrane templates.\textsuperscript{45} We chose to use the conventional hard template method for the unique advantages it offers: 1) uniformity of the nanostructures generated; 2) ease of controlling the dimensionality of the nanostructure and 3) high throughput.

Multi-segmented nanowires with two metallic ends were designed with an underlying hypothesis that the built-in metal-polymer electrical contact has lower resistance than an “out-of-wire” contact, which refers to the contact between a nanowire without metal ends and the measurement electrodes. Electrical contacts are important and need to be well understood in electronic devices like the sensor arrays. Results will be presented later on the contact measurements. Figure 2-2 shows a designed nanowire assembled in a 2-point measurement structure.

\textbf{Figure 2-2:} Scheme of a designed multi-segment nanowire assembled in a 2-point measurement structure. (Scheme drawn by Jaekyun Kim.)
A sequential deposition technique was used in the synthesis of multi-segmented nanowires. The first segment of gold was deposited in the pores of the membrane from a cyanide based plating solution. Then this segment of gold was used as part of the working electrode for electrochemical polymerization.

Electrochemical polymerization is usually performed in a solution with monomers and a supporting electrolyte under anodic conditions. A commonly accepted mechanism for electrochemical polymerization of pyrrole (Py), aniline (ANI) and EDOT is the formation of radical cations at the working electrode (anodic). Two radical cations then go through a coupling reaction, which is followed by a deprotonation process to generate...
a dimer. The dimer can lose an electron and form a radical cation again. So on and so forth the polymerization propagates. The top graph in Figure 2-3 shows the process in a simplified way. The polymer chains can be oxidized \textit{in situ} during synthesis to form positive charge carriers such as polarons and bipolarons. The anions in the supporting electrolyte are involved in the polymer to balance charges. Thus the supporting electrolyte used for oxidative electrochemical polymerization is often referred to as a dopant.

Polymerization can be performed under constant current, constant potential or through cycling potential conditions. When a new combination of monomer, solvent and electrolyte is used for nanowire synthesis, the potential cycling method is usually used first to find the threshold voltage for polymerization to initiate. For example, the bottom two graphs in Figure 2-3 show cyclic voltammograms of two kinds of nanowires. For the synthesis of PEDOT/PSS, one can see that potentials more anodic than 900 mV bring about a clearly measurable polymerization rate (bottom left graph in Figure 2-3). For the synthesis of PPy/p-toluenesulfonic acid nanowires (bottom right graph in Figure 2-3), the threshold potential is around 600 mV vs. Ag/AgCl. Potentials that are too high can introduce severe degradation or overoxidation of the formed polymer and should be avoided.\textsuperscript{48}

A problem was encountered when direct electrodeposition of Au was attempted on top of the polymer segment. Figure 2-4 shows a typical result after Au electrodeposition on PEDOT/PF\textsubscript{6}. Au penetrates into the polymer matrix. This creates a potential short circuit problem.
Experiments suggested several factors that affect this phenomenon.

(1) The morphology of the nanowire. When the nanowires have open/porous morphology, or when nanotubes are formed, the Au leakage problem is more prominent. Counterions and electrochemical conditions during polymerization affect the polymer morphology. Generally speaking, PEDOT synthesized with small counterion have more porous internal structure than those with polymeric counterions. So PEDOT/PSS was introduced to form a compact polymer to help solve the Au leakage problem. Figure 2-5

**Figure 2-4:** Au penetrates into polymer nanowires when direct electrodeposition of Au on top of the polymer segment is attempted.
shows Au-PEDOT/PSS-Au nanowires (synthesis detailed in the Experimental Section of Chapter 3) characterized by optical microscopy, TEM and FE-SEM. The polymer segment is free of continuous gold.

(2) Electrochemical conditions for metal deposition. Since the electrodeposition of Au takes a negative potential of around -900 mV vs. SCE, our hypothesis was that the polymer becomes dedoped immediately upon applying the potential. The resistance of the polymer becomes too high for Au to be plated on top of the polymer. Only solution that leaks inside the polymer can access the electrode. Therefore the metal deposition initiates at bottom of the polymer segment. If this is true, then less negative potentials should lead to a higher doping level in the conducting polymer phase and favor metal growth on top of the nanowires. We then tried electrodepositing Pt instead of Au, since Pt deposition can be carried out at less negative potential (around -350 mV vs. SCE). At this potential, the polymer might maintain a sufficient level of doping and therefore a certain degree of conductivity. This turned out to be a successful solution to this problem. Figure 2-6

**Figure 2-5**: Microscopy characterization of Au–PEDOT/PSS–Au nanowires.
shows the synthesized Au-polymer-Pt nanowires. This strategy is general and applicable to both PEDOT and PPy nanowires with various dopants.

Figure 2-6: Optical and TEM images of Au-PPy/ClO₄-Pt nanowires. Pt plating effectively solves the metal leakage problem described before.

A comparison of two samples also seems to favor this hypothesis. As will be discussed in Section 5.2, PPy/citric acid nanowires do not allow any direct Au electrodeposition above the PPy segment. In contrast, Au electrodeposition can be easily carried out on top of PEDOT/PSS nanowires directly. This can be explained by the relatively high level of conductivity known for dedoped PEDOT. In short, the doping
level and conductivity of the polymer segment seem to play an important role in the subsequent deposition of the top metal contact.

(3) Electroless deposition of Au. This technique is applicable to most of the polymer nanowires we studied. For the PPy/citric acid nanowires, after growing a short segment of electroless Au, further electrochemical plating of Au can be achieved. For PEDOT nanowires with various counterions, this helps minimize the Au leakage. An example is shown in Figure 2-7. We optimized the experimental conditions and found a relationship between the pH of the plating solution and the deposition results. The details of the electroless deposition are described in the Experimental Section of Chapter 3. In general, the Au formation kinetics are greatly influenced by the pH of the solution in the last step. At \( \text{pH} \geq 10 \), it usually takes over 24 hours to form visible gold. At \( \text{pH} < 4 \), gold forms within minutes or seconds. However, under the latter conditions, most Au precipitates in the solution instead of on the polymer nanowires. So it should be avoided. The optimal pH of 5-6 ensures relatively quick Au formation preferentially on the polymer.
2.2.2 Electrical Properties and Chemical Sensing

Electrical contact needs to be understood first before any electrical transport or chemical sensing data can be interpreted properly. Contact resistance and electrical properties were measured on individual nanowires after aligning them onto lithographically defined test structure by an electric-field assisted fluidic assembly method. Figure 2-8 shows two-point measurement data from a typical Au-PEDOT/PSS nanowire and a typical Au-PEDOT/PSS-Au nanowire. In the bias range of -3 to 3V, the current from the former is below the instrument (Agilent 4155A) detection limit. However, the I-V plots of the PEDOT/PSS nanowires with two Au ends are linear. This appears to support our hypothesis that “built-in” contacts are better than “out-of-wire” contacts.

Figure 2-7: Optical images of Au-PEDOT-Au nanowires. In the left image, direct electrodeposition of Au was applied. In the right image, an electroless deposition step was used before the electrodeposition of Au.
Further proof came from two-point and four-point measurements on several other types of nanowires. Figure 2-9 shows the current-voltage characteristics of Au-PEDOT/ClO$_4$ nanowires and Au-PEDOT/ClO$_4$-Au nanowires (synthesis detailed in the Experimental Section of Chapter 3). In this case, even with only one metal end, the 2-point I-V plot is linear in the measurement range. However, the contact resistance is approximately 95% of the total resistance, estimated from both two and four-point measurement results. In contrast, the PEDOT/ClO$_4$ sample with two gold ends has negligible contact resistance. It is worth noting that the length of the nanowire segment used for the four-point measurement is different from that for the two-point measurement. These geometric factors were measured from microscopy and taken into account for calculating the contact resistance.
We attribute this obvious difference to two reasons. First, the “out-of-wire” contact has minimal contact area compared to the “built-in” contact. Second, during the synthesis of the top contact, the complex chemical and physical bonding between formed metal and the polymer help improve the contact at the molecular scale. Compared to a recently reported post-assembly electrochemical deposition method for making PPy nanowire-microelectrode contacts, our method brings less contamination and is more reliable. In addition, wire-to-wire reproducibility is also an issue for the post-assembly method, while this is not a big concern in the template grown nanowires.

The gas/vapor response of some nanowire samples were carried out on the single nanowire level by simply monitoring their resistance change in a two-point measurement configuration. The first characterized sample was PEDOT/PSS nanowires with two Au ends. Figure 2-10 shows their response to methanol at four different concentration levels and the calibration curve of their response to acetone, methanol and ethanol. In general, these nanowires exhibit good speed and reversibility. However, the sensitivity is not high.
compared to some of the macroscopic conducting polymer sensors. More details on sensing mechanisms and sensitivity of PEDOT nanowires will be discussed in Chapter 3.

Figure 2-11 shows the response of a PANI nanowire to 100 ppm ammonia. The sensitivity in this case is high. However, even with the nanowire geometry, the PANI sensor speed is quite low. The inset shows the data (black) and a diffusion model (red line) described by \[ \frac{X_t}{X_s} = \frac{4}{\pi} \left[ \frac{D}{l} \right]^{1/2}, \] where \( X_t \) is the amount of gas molecules absorbed at time \( t \), and \( X_s \) is the total amount of gas molecules at saturation. \( l \) is the radius of the nanowire, \( D \) is the diffusion coefficient and \( t \) is time. \( D \) was estimated to be \( \sim 2 \times 10^{-14} \text{ cm}^2/\text{s} \). This value is small compared to typical diffusion coefficients of small molecules in polymers (\( 10^{-10} \) to \( 10^{-8} \text{ cm}^2/\text{s} \)). This model assumes a planar structure for
diffusion. So this is only a very rough estimation. A diffusion model in a cylinder might be a better fit.\textsuperscript{30}

Figure 2-11: Single PANI nanowire response to 100 ppm ammonia. The inset shows the resistance increasing part of the data and the red line is a fit to a diffusion model.

We noticed that even with high contact resistance, Au-PEDOT/ClO$_4$ nanowires can respond to certain analytes in an interesting way. Figure 2-12 shows that this sample showed high selectivity to nitromethane vapor over water, methanol and several other VOCs. This was not observed for the Au-PEDOT-Au sample where the contact resistance is negligible. So the response most probably originates from the gas modulation of the contact. It is well-known\textsuperscript{53} that Schottky barriers can be utilized in sensors and in many cases exhibit better performance than chemoresistor sensors.
Nanowire sensors based on diodes and transistor configurations can be proposed as complements to the current chemoresistor configuration.

Figure 2-12: Au–PEDOT/C104 nanowire response to different concentrations of nitromethane (NM) and water vapors. Three flows for each concentration. The concentration noted on the graph is the percentage of saturated vapor pressure.

2.2.3 Integration System for Sensor Arrays

The Mayer group has made some major breakthroughs in the design and fabrication of an integrated system to individually address and measure the nanoparticles. With CMOS system integration, one can measure large arrays automatically.
Preliminary data from this integrated system showed signal-to-noise ratio improvement after averaging the signals from multiple sensors. Figure 2-14 shows the response of an Au-PEDOT/PSS-Au nanowire array to 0.7% nitromethane vapor. In graph (a), the green trace is from an individual nanowire. The signal upon exposure is hard to distinguish from the baseline noise. In contrast, after signal averaging on an array of 49 nanowires, the signal to 0.7% nitromethane can be distinguished (red trace). (b) shows

Figure 2-13: Optical microscope images of part of a 16x32 nanowire array (bottom right) with 16 row on-chip n-MOS decoder (bottom left) and a three-dimensional schematic and circuit diagram of unit structure, one transistor and one resistor. Work by Jaekyun Kim and Theresa S. Mayer.
the signal-to-noise ratio (SNR) scales with $\sqrt{n}$, (n is the number of nanowires included for signal averaging). (c) is the histogram of the SNRs from individual nanowires in the same array. One can see that the distribution is not very narrow. This could be a result of the non-uniformity of the aligned nanowires. Further characterization is the focus of current research. Whether the fluctuation in the resistance measurements are the noise of the nanowires needs to be determined. There is a possibility that the test circuit is also contributing to the fluctuation. The quantitative relationship of the SNR and the sensor numbers also will be investigated further.

**Figure 2-14:** Preliminary sensing data of a Au–PEDOT/PSS–Au nanowire array in response to 0.7% nitromethane. In (a), the green trace data on a single nanowire. The red one is the averaged signal from an array of 49. (b) shows the SNR scales with $\sqrt{n}$. (c) shows the histogram of the SNR of single nanowires in the same array.
2.3 Microspheres with Conducting Polymer Nanoshells

2.3.1 Sensor Bead Integration System

In parallel to the nanowire integration system, we have also been working on an integration system for spherical nanoparticles, which was inspired by the template-assisted assembly work pioneered by Xia et al.\textsuperscript{4,54} Figure 2-14 shows the scheme of the cross-section of a single test well in an array. The assembly process is believed to be mainly driven by the capillary force at the meniscus during solvent evaporation.\textsuperscript{4,54} This assembly and measurement system can be easily scaled up and is CMOS-compatible.

![Figure 2-15: Scheme of the cross-section of a unit well of an array with a polymer-silica core-shell sphere assembled in it.](image)

2.3.2 Synthesis and Characterization

The novel integration system described above posed a challenge on nanoparticle synthesis. The fabrication of well-dispersed, uniform spheres of the right size and appropriate electrical properties is crucial to the success of the assembly process and the final device performance. We chose core-shell spheres with an insulating core and a
conducting polymer shell as the synthesis target for a few reasons. 1) Compared to pure conducting polymer spheres, the core-shell structure offers high aspect ratio of the active material – conducting polymer, which might improve the sensor signal-to-noise ratio and response time. With e-beam lithography, the pore diameter of the test structures can be as small as 30nm. However, in the initial stage, we chose experimentally simpler contact lithography. With our current facilities, the minimum pore diameter is 2 µm. At this size range, pure polymer spheres might cause low sensing speed and other issues. The thin shell ensures short diffusion path for gas analyte molecules and has the potential for fast sensing response. 2) The insulating core serves as a mechanical support and helps define the shape of building blocks. The synthesis of insulating cores such as silica is both well-established in literature and formerly practiced in the Mallouk group for various purposes.55-57 Particles in the size range of 200 ~ 1000nm can be achieved through controlled hydrolysis of tetraethoxysilane (TEOS), first described by Stöber et al.58 In addition to the convenient synthesis, silica particles usually exhibit a narrow size distribution, are electronically insulating and easy to functionalize based on their surface hydroxyl groups.

This section discusses several methods used in the synthesis of microspheres coated with conducting polymer nanoshells. Some were modified from existing literature methods and others were originally developed.

The synthetic routes to polymer-coated colloidal particles fall into two categories: direct polymerization at the particle surface or adsorption of dissolved polymer onto the particles.59 The most elegant example of the latter is layer-by-layer (LBL) assembly.60 This strategy has a couple of obvious advantages: 1) fine control of the film thickness; 2)
diversity of materials that can be deposited. LBL deposition on colloidal surfaces has been successfully demonstrated.\textsuperscript{61, 62} Conducting polymers have been used as the depositing materials in LBL deposition on planar substrates. For example, owing to the excess sulfonic acid groups on PSS, the commercially available PEDOT:PSS polymer complex can act as a polyanion during LBL assembly to generate thin films with conductivity up to 0.1 S/cm.\textsuperscript{63, 64} One can propose composite materials of alternating conducting polymer layers and oppositely charged nanoparticle layers of a variety of materials to tailor the properties. Although we did not start from this strategy because of its time-consuming nature, this is a versatile alternative for fabricating different building blocks for cross-reactive sensor arrays in the future. In the current stage, we used several methods in the category of direct polymerization at the particle surface.

One of the earliest efforts to coat colloids with conducting polymers was reported by Armes.\textsuperscript{65, 66} Silica colloids were coated with PPy. Briefly, a silica colloidal suspension was mixed with an aqueous solution of an oxidant. Then pyrrole was injected into the mixture. Their data suggested two sides of the story. On one hand, the silica particles were all coated with a layer of PPy possibly due to the adsorption of the oxidant or monomer onto the colloidal surface. On the other hand, it revealed a problem of aggregation. The “raspberry” morphology described by the authors was actually clusters of coated silica. This method is not suitable for our system since the aggregates will certainly cause problems in the assembly process.

The Jang group developed a simple method\textsuperscript{67} to synthesize silica-PANI core-shell nanoparticles. At pH 3, aniline exists in the positively charged anilinium form and silica particles possess negative charge on their surface, since aniline has a pKa of 4.63 and
silica has an isoelectric point of 2. The strong electrostatic interaction induces an anilinium-covered silica structure, on which the polymerization is then carried out. This method generates a thin layer of PANI of less than 2 nm. This method was not chosen for the initial stage of this project since we needed a slightly thicker layer to ensure good continuity for stable electrical measurements. But it might be an ideal method in the future for our system, especially when the test structure scales down to less than 50 nm in pore diameter.

The Feldheim group developed a membrane-supported synthesis method to coat Au nanoparticles with PPy or poly(N-methylpyrrole).\textsuperscript{68-70} Briefly, citric-stabilized Au colloids are filtered through the pores of an AAO membrane. Nanoparticles are trapped in the pores because of the smaller pore diameter of the branched side of the membrane. One side of the membrane contacts an aqueous solution of the oxidant, such as Fe(ClO\textsubscript{4})\textsubscript{3}. The other is in contact with the equilibrium vapor associated with the neat liquid pyrrole. This method leads to core-shell Au-polymer spheres as is illustrated in Figure 2-15.
We slightly modified this method in the effort to achieve silica bead coating. Since the final bead diameter of about 1 µm was needed to accommodate the test bed, we started from silica beads of about 900nm in diameter. Two track-etched polycarbonate membranes (Whatman Nuclepore) were stacked together and used to support the silica beads. The top membrane had 8 µm pore diameter and the bottom one had 0.4 µm pore diameter. Silica colloids were filtered through the membranes, which were clamped in a filtration setup. 0.1M Fe(ClO₄)₃ solution was poured on top of the membrane. The bottom of the membranes was in contact with pyrrole vapor evaporated from a reservoir of neat liquid pyrrole. After 15 minutes reaction time, the setup was disassembled and silica beads on the membranes were collected and rinsed with methanol.

Figure 2-16: TEM image of Core-shell Au-PPy nanoparticles synthesized by Feldheim et. al.
**Figure 2-17**: TEM images of: PPy-coated silica particles synthesized by a membrane-supported method (top) and silica beads without coating for comparison (bottom).
This procedure resulted in interesting structures. Instead of uniform coating achieved in the Au nanoparticle case shown in Figure 2-16, the silica beads seem to be covered by a single layer of polymer spheres of about 50nm diameter (Figure 2-17). The difference is possibly caused by the different interactions between pyrrole and the two kinds of particles. Feldheim et al. suggested\textsuperscript{70} PPy growth started from nucleation on the surface of the Au nanoparticles. If that is true, then in our system, the nucleation seems to happen at the center of the small PPy nanospheres instead of on the silica surface. The interaction between pyrrole/PPy nitrogen and Au is probably important for the nucleation process. The phenomenon that the formed PPy nanoparticles tend to surround the silica microsphere can be attributed to the electrostatic interaction between the positively charged PPy nanoparticles formed and the negatively charged silica microspheres. Chemically synthesized PPy nanoparticles in the diameter range of 17 to 59 nm were reported\textsuperscript{71} to have an isoelectric point of around 8.5. So in a broad range of pH (2 ~ 8.5), there should strong electrostatic interaction between PPy nanospheres and silica microspheres.

This method is promising for fabricating core-shell building blocks. The current yield (number of beads with a complete layer of coating/total number of beads) is low (about 10-20%). Many silica beads remain bare or only have a small amount of PPy on the surface, e.g. the beads on the upper right corner of the top graph in Figure 2-16. But further optimization of the experimental conditions could lead to higher yields.

The Matijevic group discovered that pyrrole can polymerize on the surface of oxide nanoparticles without using electrochemistry or adding a solute oxidant.\textsuperscript{72-74} The reaction usually takes more than 24 hours and temperature as high as 100 °C. It was
proposed that oxygen is the major oxidant that initiates the polymerization of pyrrole. IR studies suggested that the polymer generated from this method contains the overoxidation product pyrrolidinone, which breaks the conjugation and leads to polymers of very low conductivity or nonconducting polymers. So this method is not suitable to fabricate building blocks with appropriate electronic properties.

Foulger et al. developed a method to coat commercially available colloidal silica (SNOWTEX-ZL from Nissan Chemical).\textsuperscript{75, 76} We repeated the procedure they described. In a typical synthesis run, 6 g SNOWTEX-ZL silica beads were suspended in 140 mL DI water. 0.327 mL EDOT (Aldrich) dissolved in 40 mL methanol was added to the silica dispersion. The mixture was stirred for 2 hours. Then 1.81 g ammonium persulfate (oxidant) dissolved in 20 mL water was added. The reaction mixture was kept at 30 ºC for an appropriate reaction time with 500 rpm stirring.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2-18}
\caption{TEM images of SNOWTEX-ZL before coating (left) and SNOWTEX-ZL after coating with PEDOT using Foulger’s method.}
\end{figure}
The TEM analysis does not show an obvious polymer coating with different contrast from that of the silica cores. This is possibly due to the different morphology of Stöber silica beads and SNOWTEX-ZL beads. Stöber silica beads have very smooth edges (see the bottom graph in Figure 2-16 for an TEM image). In contrast, the edge of SNOWTEX-ZL beads seems rough (Figure 2-17 left). This might be the result of a porous morphology. With a porous morphology, the electron density is lower, which might coincide with the polymer electron density, which could cause the polymer layer non-distinguishable from the silica core. However, further analysis points to the existence of a layer of polymer material on the surface. The size distribution measurement results are shown in Figure 2-18. After coating, the peak diameter increase from 170 nm to 220 nm. The measurements were carried out on a Malvern Zetasizer Nanosizer S. However, the slight increase in diameter measured by this method could also be a result of aggregation or the formation of polymer particles. It is not a definitive way to determine the existence of a polymer and only used as an auxiliary method.
Figure 2-19: Nanoparticle size distribution. SNOWTEX-ZL silica colloids (top) and SNOWTEX-ZL after Foulger’s PEDOT coating method (bottom).
As another auxiliary method, Zeta potential measurement was performed. The results also seem to support the existence of a polymer layer. Before coating, the zeta potential was -43. After coating, the zeta potential became less negative with a value of -30. The conducting polymer coating decreased the net negative surface charge of silica. A Brookhaven ZetaPALS Zeta Potential Analyzer was used for these measurements.

The most convincing evidence is from TEM study of the PEDOT coated silica after etching the silica core in a 24% HF solution for one minute. Figure 2-19 shows empty shells left after etching. With reaction time increasing, the shell thickness seems to increase too. The left graph in Figure 2-19 shows the shells from the products after 20 hours reaction time. 48 hours reaction time yielded thicker shells with better defined spherical shape as is illustrated by the right image in Figure 2-19.
Foulger’s method generates core-shell beads with the diameter of 100 ~ 200 nm based on the starting materials diameter. However, this method cannot be successfully transferred to the Stöber silica beads. Figure 2-20 shows the experiment results on Stöber silica beads of diameter around 900 nm. Dissolving the core did not result in polymer shell. The proposed mechanism\textsuperscript{75,76} of Foulger’s method is the adsorption of EDOT onto the silica surface before polymerization. The SNOWTEX-ZL sample appears to be a better adsorption substrate for EDOT than Stöber silica beads.

**Figure 2-20:** TEM images of the empty PEDOT shells after dissolving SNOWTEX-ZL silica core in hydrofluoric acid. Original core-shell sample prepared by Foulger’s method. The images on the left were taken on a sample prepared after 20 hours EDOT polymerization time. The image on the right was taken on a sample prepared after 48 hours EDOT polymerization time.
New methods are needed to achieve complete and uniform coating on Stöber silica particles with less aggregation and higher yield. The first method we developed in our lab is based on the strong interaction between Fe$^{3+}$ and silica surface. In order to prevent the aggregation problem, the free oxidant concentration in the solution is minimized. The procedure is as follows: 20 mg silica beads of about 900 nm diameter were suspended in 40 mL water. 38 mg FeCl$_3$ was added to the colloidal suspension. 30 minutes stirring was followed by 5 washing cycles (each washing cycle contains three steps: centrifuge, remove supernatant and re-disperse the particles in water) to remove the free FeCl$_3$ from the aqueous solution. Then pyrrole was added to start the polymerization process. Figure 2-21 shows the typical coated beads. This method yielded uniform silica particles with no aggregation. However, PPy does not seem to form a complete

Figure 2-21: TEM image of PEDOT-coated Stöber silica particles synthesized with Foulger’s method.
continuous layer. Pyrrole concentration was varied and no obvious effect was observed on the coating results. Further optimization could promote the adhesion of Fe$^{3+}$ to the silica surface.

![TEM image of silica particles with discontinuous PEDOT coating.](image)

**Figure 2-22:** TEM image of silica particles with discontinuous PEDOT coating.

The second method we developed involves a nonpolar solvent, hexane. Since FeCl$_3$ has very poor solubility in hexane, we expected to minimize the amount of oxidant in the medium by introducing hexane. 15 mg silica particles of about 900 nm diameter were dispersed in anhydrous hexane. 1 mg ~ 3.5 mg FeCl$_3$ was quickly weighed and added. After strong sonication, the reaction mixture was put on a magnetic stirring system. Under vigorous stirring, 6.8 uL EDOT was added. The reaction mixture turned
from light yellow to green in a few minutes. After 30 minutes, the colloids were collected by centrifuging and washed with methanol for a few cycles.

Figure 2-23: FESEM (a) and TEM (b and c) images of core-shell silica-PEDOT spheres synthesized in hexane.

This method yielded nanoparticles with continuous coatings. Figure 2-22 shows the contrast of the polymer layer with silica core under TEM. The thickness of the film can be controlled to some extent by varying the amount of FeCl$_3$ added. Figure 2-22b shows a thick coated bead when 3.5 mg of FeCl$_3$ was added. Figure 2-22c shows that the
coating layer is much thinner when only 1 mg FeCl₃ was used. There is minimal aggregation. And the yield was good (about 50%). So it was chosen as the first generation of spherical building blocks for the assembly and measurements.

We propose a possible mechanism for the method described above. Since the silica spheres were stored in air before use and the hygroscopic FeCl₃ was weighed in air, there is small amount of water involved in the process. Water molecules prefer to reside near the hydrophilic surface of silica particles since the medium hexane has very poor miscibility with water. The oxidant FeCl₃ is very well soluble in water and does not dissolve in hexane. So after strong sonication, FeCl₃ is distributed in the aqueous layer around the silica spheres. Then the hexane-soluble monomer EDOT was added. The reaction happens only at the interface of water and hexane, which affords the coating and minimizes the amount of free polymer in the suspension. A similar experiment was carried out in a glove box after complete removal of moisture from the silica. No coating around the silica beads was formed. This supports our proposed mechanism. However, we do not exclude the possibility of other mechanisms.

2.3.3 Electrical Properties and Chemical Sensing Performance

With the integration system described in 2.3.1, core-shell silica-PEDOT spheres made in hexane using the above method have been assembled, individually addressed and measured in collaboration with Jaekyun Kim in the Mayer group. Figure 2-23 shows the I-V characteristics of a typical PEDOT-coated silica sphere. It exhibits nonlinearity in the range of -0.5V to 0.5V. Nonlinearity could come from electrical contact or the polymer
itself (See Section 3.2.1.2). The physically entrapped beads can be viewed as analogous to the nanowires without built-in contacts aligned in an electric field (Section 2.2.2). It is likely that the contact takes a significant part in the overall resistance. However, one should not completely rule out the other possibility either. When the field increases, the existing conducting mechanism can be affected or more conduction paths could be created.\textsuperscript{77} Nonlinearity is common for hopping-dominated systems at low temperature and high electric field.\textsuperscript{78} Overall, the nanowire platform seem to be more favorable than the bead platform in the sense that the contacts in the nanowires can be characterized more conveniently with four-point measurements and it is easier to construct “built-in” contacts in the nanowire configuration.

Comparison between control experiments shows that the current indeed comes from the PEDOT coating. Figure 2-23 shows the I-V comparison of the core-shell sample with an empty well and a pristine bare silica bead. The I-V characteristics from the beads are very stable. On the bottom graph, the black line shows the I-V plot of the first measurement. And the red line shows the result from the tenth measurement. They basically overlap with each other.
Figure 2-24: The top graph shows the I–V characteristics of a PEDOT-silica core-shell sphere plotted on the linear scale. The inset shows an optical microscope image of the top view of a core-shell sphere assembled in a test “well”. The bottom graph shows the I–V characteristics of the same PEDOT-silica core-shell sphere plotted on a semi-logarithmic scale (black line). I–Vs measured on pristine silica beads (blue line) and empty wells (green line) are also shown on the bottom graph.
Responses of the PEDOT-coated beads to several gases/vapors have been measured. Results on water, methanol and hydrogen sensing are shown in Figure 2-24. Despite the nonlinearity in the I-V plots, one can still extract the resistance from the low bias region. The resistance increases upon gas exposure. The sensing mechanism could be the modulation of the contact resistance as well as the polymer resistivity (see Section 3.2.1.3 for more discussion on sensing mechanisms).

As a preliminary step, we have demonstrated a CMOS-compatible assembly system for spherical particles.

A method is proposed to include built-in barcodes in the silica cores before surface functionalization with conducting polymer or other materials. The idea is to add optical signatures to different sensing elements for the multiplexing needs in the future. Silica beads can be synthesized in a “layer by layer” fashion according to a reported method. Dye molecules can be trapped in each individual layer or a combination of layers. Preliminary experiments (detailed in the Experimental Section of this chapter) showed that three-layered silica beads (1) with dyes only in the outer layer, (2) with dyes only in the middle layer and (3) without dyes, can be easily distinguished from fluorescence and bright field optical microscope (Figure 2-25). In principle, one should be able to achieve several different optical signatures with just one dye species. Since dye molecules are included throughout the thickness of the designated layer/layers, the fluorescence intensity is higher, which makes detection convenient. This proposed method could also be of interest in the field of suspension arrays.
Figure 2-25: Responses of individual beads to three analytes.
Figure 2-26: Proposed barcoding strategy for silica spheres synthesized with a “layer by layer” method. The three images/scheme on the left show the silica particles with dye molecules only in the outer layer. The diameters of the beads appear the same in the optical and fluorescence microscope. The ring shape of the particles in the fluorescence image confirms that the dye molecules are only present in the outer layer and not in the two inner layers. The three images/scheme in the middle show the silica particles with dye molecules only in the middle layer. The diameters of the beads seem bigger in the optical microscope than in the fluorescence microscope. The three images/scheme on the right show the silica particles without dye molecules.
2.4 Experimental

Procedure to fabricate layered silica beads with fluorescence barcodes.

20mL ammonium hydroxide mixed with 100mL ethanol. Separately, 0.5 ml tetraethoxysilane (TEOS) was mixed with 2mL ethanol. Then this TEOS/ethanol mixture was added quickly to the ammonium hydroxide solution under stirring. Reaction was under stirring for 4.5 hours. Then divided into two halves in order to make two types of beads with dyes in the outer layer only and the middle layer only. The first half added the mixture of 4mL TEOS and 16mL ethanol drop by drop (within 15min). Then after 2 hours, added 28mg Rhodamine 6G perchlorate, sonicated and stirred till dye dissolve. Then added the mixture of 4mL ammonium hydroxide and 16mL ethanol drop by drop within 15min. Overnight. The second half added 22mg the same dye, stirred and sonicated till dye dissolved. Then added the mixture of 4mL ammonium hydroxide and 16mL ethanol drop by drop within 15min. After reaction time of about 2 hours. Washed off the dye by two centrifuge and resuspension cycles. Then the spheres were resuspended in 40mL ethanol and then added the mixture of 10mL TEOS and 30mL ethanol. Then the mixture of 4mL ammonium hydroxide and 16mL ethanol was added drop by drop within 15min to the pink suspension. Overnight.

2.5 Conclusions

In conclusion, building blocks of anisotropic multi-segmented nanowires, core-shell spherical nanoparticles have been synthesized and assembled into CMOS-compatible integration systems. New synthetic methods have been developed for the
fabrication of these building blocks. Built-in contacts seem to be a useful strategy to
decrease the contact resistance between nanowires and electrodes. The chemical sensing
data showed good reversibility and speed of individual nanosensors. The sensitivity needs
to be improved, possibly by introducing receptor groups for desired analytes. Preliminary
data from CMOS arrays showed some signal to noise ratio improvement. More careful
characterization of the integration system, optimization of the sensing elements and
development of cross-reactive arrays are currently under investigation.

2.6 References

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Chapter 3

Electrical Transport and Noise Characteristics of PEDOT Nanowires

3.1 Introduction

The last decade has witnessed rapid growth in research on conjugated polymer nanostructures, which has been driven by their unique optical, electrical and mechanical properties as well as their processing and cost advantages. The potential applications of conducting polymer nanostructures have been recently reviewed. Poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires and nanotubes have been proposed as active materials for ultrafast electrochromics and field emission displays. Nanoresistors, diodes and field-effect-transistors based on polypyrrole (PPy) nanowires have been demonstrated. The possibility of using conducting polymer nanorods grown by the hard template method as biosensors has also been explored.

While the synthesis and applications of conducting polymer nanostructures have received considerable attention recently, there have been relatively few fundamental studies on their electrical transport properties. We have been working with conjugated polymer nanostructures, and particularly template-grown PEDOT nanowires, as building blocks for chemoresistive gas sensor arrays. In this application, it is important to understand the charge transport mechanisms that influence the electrical conductivity and vapor sensing properties of these nanowires. Despite much experimental data, the details of the transport mechanisms are still a matter of debate, especially for PEDOT
nanowires. The electronic behavior is complex and appears to depend on the structure of the polymer, which in turn depends on the synthesis conditions, doping level, charge balancing ions, and other factors, such as the nature of the contacts.

This chapter presents data showing that there is a prominent difference in the charge transport mechanisms of PEDOT/PSS and PEDOT/ClO$_4$ nanowires. Temperature-dependent resistivity measurements show that these nanowires are on the insulating and metallic side of the metal-insulator (M-I) transition, respectively. Consequently, they exhibit quite different properties in vapor sensing. Possible sensing mechanisms are proposed based on the structural information implied by the transport data.

In addition to the average resistance, the resistance fluctuation, or electrical noise, is another important parameter for two reasons. First, it is critical for device performance. For example, low noise level is usually desired for electronic devices such as diodes and transistors. In sensors, signal to noise ratio essentially decides the lower detection limit$^{12}$. Second, since resistance involves the second moment of the current distribution, while noise involves the fourth moment, the noise is expected to be more sensitive than average resistance to any change in current distribution and thus more informative about the underlying transport mechanism.$^{13, 14}$ For the above reasons, noise study in other materials have been decades long. The $1/f$ noise in semiconductors and metals has been well understood.$^{15, 16}$ The intensive research in the last few years on the $1/f$ noise from carbon nanotubes$^{17-19}$ has yielded quite good comprehension. However, the noise in conducting polymers is a relatively new area. Only a few reports on the noise from conducting polymer field effect transistors (FETs)$^{20}$ and film resistors$^{21, 22}$ are noticeable. To the best of our knowledge, no experimental data of the electrical noise in one-
dimensional conducting polymer nanostructures have been reported. Thus we have also been investigating the noise characteristics of template-grown PEDOT samples mentioned above.

3.2 Results and Discussion

3.2.1 Electrical Transport in PEDOT Nanowires

A typical nanowire in our study consists of three segments: two gold ends and a conducting polymer part in the middle. The nanowire synthesis was carried out using a sequential deposition technique in anodic aluminum oxide membrane templates (see Experimental section of this chapter for details). The dark-field optical microscope and transmission electron microscope (TEM) images of the nanowires are shown in Figure 3-1a. The two materials can be distinguished clearly in both images because of the high electron density and reflectivity of the gold segments.
Individual nanowires were aligned in a four-point measurement test bed shown in Figure 3-1b using an electric-field assisted fluidic assembly method. The two inner electrodes were fabricated by electron-beam lithography and liftoff of a 10 nm Ti / 70 nm Au thick metal electrode deposited by thermal evaporation. Four-point measurements were carried out by monitoring the voltage drop between the two inner electrodes while applying a DC current between the two outer electrodes. A comparison of two-point and four-point resistance shows that the contact resistance between the gold ends and the PEDOT is negligible in these nanowires.

The diameters and lengths of the aligned nanowires were estimated from the FE-SEM images. The average room temperature conductivity of PEDOT/PSS nanowires is ~ 5 S/cm, which is slightly lower than the 80 S/cm of electrodeposited PEDOT/PSS films reported in the literature possibly due to partial dedoping of the nanowires during the synthesis of the second Au end. The average room temperature conductivity of PEDOT/ClO₄ nanowires is ~ 200 S/cm.

Figure 3-1: (a) Optical and TEM (inset) images of multi-segmented Au-PEDOT/PSS-Au nanowires. (b) Field emission scanning electron microscopy (FESEM) image of a Au-PEDOT/PSS-Au nanowire aligned on the test circuit with four Au electrodes.
3.2.1.1 The Temperature Dependence of Resistivity

The temperature dependence of the resistivity has been used extensively to probe the charge transport mechanisms of conducting polymers.\textsuperscript{24} Recently, Kaiser reviewed\textsuperscript{25} the electrical transport properties in a broad range of conducting polymer films. A fluctuation-induced tunneling model can be used to describe most highly conducting samples, while hopping typically dominates in less conductive films. Hopping transport leads to a rapid increase in resistivity with decreasing temperature. In the critical regime near the metal-insulator (M-I) transition, the temperature dependence of the resistivity follows a power law. In general, the macroscopic charge transport mechanism is determined by the coexistence and distribution of crystalline domains and disordered regions as well as the doping level.

The current-voltage (I-V) characteristics of both types of nanowires were measured over a temperature range from 5 to 300 K. At temperatures above 30 K, both types of nanowires exhibit ohmic behavior. The temperature dependence of the low bias resistance of the PEDOT/PSS and PEDOT/ClO\textsubscript{4} nanowires is illustrated in Figures 3-2a and b, respectively. For the PEDOT/PSS nanowires, the resistivity ratio $\rho(20 \text{ K})/\rho(300 \text{ K})$ is $\sim 300$. The data in the temperature range from 20 to 300 K can be best described by Equation 3.1, as shown in Figure 3-2a,

$$R(T) \propto \exp\left[(T_0 / T)^{1/2}\right]$$

Equation 3.1

where $T_0$ is between 1000 to 2000 K for different nanowires in this sample. This same temperature dependence and comparable values of $T_0$ were observed for PEDOT/PSS thin films having conductivity similar to that of our nanowires.\textsuperscript{10} The
saturation of the resistance at lower temperatures may be explained by the dominating role of tunneling effects in the conductivity when thermal excitation fails to support hopping.

Figure 3-2: (a) Temperature dependence of the low bias resistance of a PEDOT/PSS nanowire. The straight line is a fit to Equation 3.1. (b) A log-log plot of the temperature dependence of the resistance of a PEDOT/ClO₄ nanowire, which follows a power law at high temperatures (shown by the straight line).

In contrast, the PEDOT/ClO₄ nanowires have a resistivity ratio $\rho(20 \text{ K})/\rho(300 \text{ K}) < 2$. As is shown in Figure 3-2b, the resistivity in the temperature range from 20 to 300 K follows a power law, which is typically used to describe the critical regime of the M-I transition. A similar temperature dependence was observed in highly-conducting electrochemically deposited PEDOT thin films doped with PF₆, BF₄, and CF₃SO₃.²⁶
The insulating, critical, or metallic state can be further determined from the slope of the temperature dependence of the reduced activation energy $W$, which is given by $W = d\ln(\sigma(T))/d\ln(T)$. Positive, zero and negative slopes of the $W-T$ plot correspond to the metallic, critical, and insulating regimes, respectively. As shown in Figure 3-3, the PEDOT/PSS nanowire is in the insulating regime with a slope from the log($W$)-log($T$) plot of $\sim -0.5$ (see inset of Figure 3-3). The nearly temperature independent $W$ of PEDOT/ClO$_4$ nanowires is characteristic of the critical regime, and its value of around 0.2 indicates that these nanowires are slightly on the metallic side of the M-I transition.

Figure 3-3: The reduced activation energy $W$ for two nanowire samples.
The temperature dependence of the resistivity given by Equation 3.1 follows from different models, which all take into account a hopping or variable range hopping (VRH) mechanism. The quasi 1D Mott insulator model\textsuperscript{28} assumes that VRH along one direction dominates and $T_0$ is approximately\textsuperscript{29} $B_1/k_B N(E_F) a$, where $N(E_F)$ is the 1D density of states, $a$ is the localization length, and $B_1 > 1$ is a percolation constant. Taking $N(E_F)$ to be about 0.5 eV\textsuperscript{-1} per three-ring PEDOT unit\textsuperscript{30} and $a$ to be about the length of the three-ring unit, we obtain $T_0 \geq 23,000$ K. This is much higher than the experimentally measured values, and thus it is unlikely that this model can be used to describe charge transport in our PEDOT/PSS nanowires.

Shklovskii and Efros\textsuperscript{31} considered 3D VRH with the Coulomb gap at the Fermi level. In this model, the localization length is given by the equation\textsuperscript{31} $a = \frac{2.8 e^2}{k_B T_0 \kappa \varepsilon_0}$, where $e$ is the electron charge, $\kappa$ is the dielectric constant, $\varepsilon_0$ is the permittivity of vacuum, and $k_B$ is the Boltzmann constant. Using the experimentally obtained $T_0 = 1000$ K and the typical dielectric constant $\kappa \sim 2$ for conducting polymers, we obtain $a \sim 0.3$ μm, which is physically unreasonable, since a typical value of this localization length in conducting polymers does not exceed tens of nanometers.\textsuperscript{24} Furthermore, this model is usually applicable at low temperatures in disordered semiconductors, where the transport at higher temperatures is characterized by the 2D or 3D variable range hopping.\textsuperscript{32}

There are several other models that predict the temperature dependence of the resistivity in the form of Equation 3.1. For example, the model of Klafter and Sheng\textsuperscript{33} for granular conductors takes into account the distribution of grain sizes, while that of Zuppiroli\textit{ et al.}\textsuperscript{34} describes hopping between polaronic clusters. Zuppiroli’s model
assumes variations in dopant distribution. We do not have strong experimental evidences to distinguish between these two models. However, although these two models are based on different microscopic structures, both of them describe hopping between more conducting domains embedded in an insulating matrix.

The charge transport mechanisms that determine the electrical conductivity of the nanowires are determined by the microscopic structure of the conducting polymer, which in turn originates from the synthesis conditions. The difference in the electrical transport properties of our PEDOT/PSS and PEDOT/ClO₄ nanowires most likely comes from the different counterions and solvent effects. Similar phenomena were observed in PPy thin films having different counterions.³⁵ With the size of the counter ions increasing (from hexafluorophosphate to p-toluenesulfonate to sulfonated poly(hydroxyether)), the conductivity decreased and the temperature dependence became stronger. Larger counterions are believed not only to increase the spacing between conjugated chains, but also to increase the conformational disorder.³⁵ As a result, polymers with polyanionic counterions are less crystalline than polymers doped with smaller counterions. Another possible factor is the solvents used in the electrochemical synthesis. Acetonitrile is used in the synthesis of PEDOT/ClO₄, while 1:1 vv acetonitrile/water is used for PEDOT/PSS synthesis because of the poor solubility of PSS in pure acetonitrile. It is known that aprotic solvents such as acetonitrile increase the integrity of the synthesized polymers because it minimizes nucleophilic reactions³⁶ that terminate chain propagations.
3.2.1.2 Nonlinearity in PEDOT/PSS nanowires

The temperature-dependent I-V characteristics are symmetric for both types of conducting polymer nanowires. Figure 3-4 shows I-V plots of a PEDOT/PSS nanowire measured at 30, 20, 10, and 5 K. The nanowires exhibit ohmic behavior at low electric field and/or high temperature. When the temperature decreases below 30 K, the I-V characteristics become nonlinear. In contrast, the PEDOT/ClO$_4$ nanowires are ohmic over the experimentally measured range of temperatures and fields. Schottky barriers are a common source of nonlinear I-V behavior. However, the influence of metal-polymer contacts on the conduction is eliminated by using the four-point measurement test structure. Thus, it is possible to exclude Schottky emission as the source of the nonlinearity we observed for the PEDOT/PSS nanowires.
From the inset in Figure 3-4, the logarithm of the nonlinear part of the resistance is proportional to the electric field $F$ inside the sample: $\Delta \ln(R) \sim F$. A similar electric field dependence was obtained by Pollak and Riess\textsuperscript{37} for the Mott insulator in the 2D and 3D VRH regime and by Shklovskii and Efros\textsuperscript{38} for the 3D VRH regime with a Coulomb gap. Both predicted that the electric field dependence of the resistivity in the intermediate field regime is described as,

$$\ln R = \ln R_0 + \frac{eFL}{k_B T}$$

Equation 3.2

where $R_0$ is the low-field resistance, $T$ is the sample temperature, $k_B$ is the Boltzmann constant, and the characteristic length $L$ is on the order of the hopping distance. The hopping distance in these models is temperature dependent and increases as

Figure 3-4: I–V characteristics of a single PEDOT/PSS nanowire at three different temperatures. The inset shows the field dependence of the nanowire resistance at 10 K.
the temperature decreases. Based on the previous discussion regarding the temperature
dependence of the resistivity, it is unlikely that either of these models can explain the
nonlinearity observed in our PEDOT/PSS nanowires. Nevertheless, Equation 3.2 can be
used phenomenologically where is considered to be a physically relevant characteristic
length. In the region where the temperature dependence of the conductivity follows
Equation 3.1, the characteristic length is nearly temperature independent and is in the
range of few nanometers, which is a reasonable distance for hopping in PEDOT/PSS
conducting polymers.39

3.2.1.3 Transport Mechanisms and Chemical Sensing Properties

Like their macroscopic counterparts, each individual nanowire can function as a
chemoresistor to transduce the polymer-analyte interaction into a detectable physical
signal. The resistance change of individual nanowires is easily monitored and used as a
sensing signal. In general, the nanowires exhibit good reversibility and short response and
recovery time upon exposure to water and methanol vapors. Using the definition of 90%
of resistance change, the response time and recovery time for PEDOT/PSS are both less
than 20 seconds. For PEDOT/ClO₄ the response and recovery occur within 40 seconds.

Figure 3-5 illustrates pronounced differences in the sensing behavior of the two
types of nanowires to water and methanol vapors. Both water and methanol vapor induce
a decrease in the resistivity of PEDOT/ClO₄ and an increase in the resistivity of the
PEDOT/PSS nanowires. We propose different sensing mechanisms for the two types of
nanowires. For PEDOT/ClO₄ nanowires, the decrease in resistivity upon solvent vapor
exposure possibly results from the partial charge transfer mechanism.\textsuperscript{40} Josowicz et al. have proposed this mechanism to explain the sensing behavior of conducting polymers. According to this theory, the difference between the polymer Fermi level $E_f$ and the Mulliken electronegativity $E_\eta$, which is defined as the average of its electron affinity and its ionization potential, measures the “driving force” for the weak intermolecular partial charge transfer. The direction of the charge transfer can be inferred from the sensing data. Both water and methanol accept partial electron transfer from the polymer. Thus, the work function/charge carrier numbers and the conductivity of PEDOT/ClO$_4$ are increased.

As discussed above, the charge transport in PEDOT/PSS nanowires appears to be dominated by hopping between metallic, or highly conducting islands embedded in an insulating matrix. In that case, the simplified model of partial charge transfer is not adequate to explain the interaction between vapors and PEDOT/PSS, since the insulating or less conducting regions play an important part in the conduction process. Charlesworth et al. explained their sensing data\textsuperscript{41} by modeling the hopping process as an electron-transfer reaction as it occurs in electrochemistry. According to this model, adsorption of solvent vapor increases the resistivity of PPy by decreasing the hopping rate. Solvents with larger dielectric constants decrease the hopping rate more than those with smaller dielectric constants. A complementary mechanism for explaining the resistance increase of PEDOT/PSS upon exposure to solvent vapors is the swelling of the polymer. Swelling increases the hopping distance for charge carriers and thus lowers the conductivity.\textsuperscript{42} Both mechanisms predict that the resistance should increase with increasing pressure of almost all volatile organic compounds (VOCs). We did observe this behavior with
PEDOT/PSS nanowires in response to water, methanol, ethanol, isopropanol, pentanol, acetone, acetonitrile, dichloromethane, etc.

Figure 3-5: Vapor response of individual PEDOT/ClO₄ and PEDOT/PSS nanowires to water and methanol. The starting point of the vapor flows are marked by “W” (water) and “M” (methanol). “N” indicates the time when nitrogen purging starts. The inset in the top left graph shows the response of a PEDOT/ClO₄ nanowire to low concentrations of water vapor. The vapor concentrations are marked on the graphs. The units are all “ppm”.

Figure 3-5 also shows that there is a significant difference in the signal-to-noise ratio between the two kinds of nanowire sensors. PEDOT/ClO₄ offers a much lower baseline noise level than PEDOT/PSS, which leads to better sensitivity and lower
detection limit. In fact, a single PEDOT/ClO$_4$ nanowire can detect water vapor in the range of few tens of ppm, close to the best conducting polymer sensors in the literature.$^{42, 43}$ The inset in the “ClO$_4$/water” graph in Figure 3-5 shows the clear response of a PEDOT/ClO$_4$ nanowire to 130 ppm and 260 ppm water vapor.

The logical next step to optimize the sensing performance of PEDOT/ClO$_4$ nanowires would be (1) to maximize the sensing signal through the adjustment of the polymer doping level or the driving force for partial charge transfer; and (2) to minimize the electrical noise. Under the assumption that the noise is caused by the structural disorder, one can possibly achieve lower noise nanowire sensors through low temperature electrochemical synthesis, which is known$^{36}$ to be an effective way to minimize the structural disorder in conjugated polymers.

3.2.2 Electrical Noise Characteristics of PEDOT Nanowires

Since electrical noise essentially determines signal-to-noise ratio in gas sensor devices, it should be informative to investigate the noise characteristics of both PEDOT/PSS and PEDOT/ClO$_4$ nanowires. As discussed above, at low temperature and/or high electric field, I-V plots of PEDOT/PSS nanowires exhibit nonlinearity. In a nonlinear inhomogeneous system like most conducting polymers, noise usually exhibits different characteristics in the linear and nonlinear regimes.$^{14}$ In this study, we focused on the linear regime for simplicity. Also, the low field, room temperature linear regime is more relevant to the potential applications of conducting polymer nanowires in electronic devices. The noise measurement system was designed and set up by Dr. Alexey E.
Kovalev in the Mayer group. Details of the setup are described in the Experimental Section.

3.2.2.1 Frequency Dependence

The frequency dependence of the noise for both types of nanowires follows the usual 1/f law. Figure 3-6 depicts the low-frequency current noise power spectrum at different bias levels across a single PEDOT/PSS nanowire. Background noise at zero bias is orders of magnitude lower than the excess noise in the frequency and bias ranges we used and thus neglected for the calculation of the noise power $\beta$. Power law fitting of the data yields $\beta=1.05 \pm 0.03$ on multiple individual PEDOT/PSS nanowires. 1/f noise is believed to result from the superposition of many fluctuators with a distribution of time constants.$^{15,16}$ The physical origin of 1/f noise varies for different systems.
In the measurement range, noise is proportional to $V^2$. The inset in Figure 3-6 shows the results from a typical PEDOT/PSS nanowire for three values of applied bias. The inset shows the variation of $\beta$ for the sample set. The inset shows the second power dependence on the applied bias of $S_i$ at 1Hz.

Figure 3-6: Current noise power $S_i$ vs. frequency for a PEDOT/PSS nanowire for three values of applied bias. The inset shows the variation of $\beta$ for the sample set. The inset shows the second power dependence on the applied bias of $S_i$ at 1Hz.

In the measurement range, noise is proportional to $V^2$. The inset in Figure 3-6 shows the results from a typical PEDOT/PSS nanowire. The voltage dependence is believed to be indicative of whether the noise is a result of equilibrium resistance fluctuation (second power) or a driven phenomenon (exponent \( \neq 2 \)).\(^{14}\) So within our measurement range, the noise in the PEDOT nanowires can be ascribed to equilibrium resistance fluctuation. It is not a bias-driven phenomenon.

With the frequency and voltage dependency established, we can use a coefficient $A$ to characterize the absolute amplitude of the 1/f noise. $A$ is defined as:

$$S_i = AI^2 / f^\beta$$  \hspace{1cm} \text{Equation 3.3}
3.2.2.2 Comparison of Noise of PEDOT/ClO$_4$ and PEDOT/PSS Nanowires

The difference in the noise of PEDOT/ClO$_4$ and PEDOT/PSS nanowires first discovered in the sensing experiments (see Figure 3-5) was further confirmed by power spectral density measurements. Figure 3-7 shows normalized data from the two types of nanowires. The noise coefficient $A$ can be estimated from the value at 1 Hz. For PEDOT/PSS and PEDOT/ClO$_4$ nanowires, $A$ is $4.5 \times 10^{-7}$ and $3.0 \times 10^{-8}$ respectively. So the noise of PEDOT/PSS nanowires is more than one order of magnitude larger than that of PEDOT/ClO$_4$ nanowires. The charge carrier density is likely to be different in the two samples. Polymeric counterions usually induce a larger spacing between conjugated polymer chains and induce conformational disorder.$^{35}$ These could contribute to the higher noise level in the PEDOT/PSS sample. However, a better understanding of the noise generation mechanisms in these systems is needed before a definitive explanation can be proposed.

To compare with other materials, it was reported$^{44}$ that high quality metal films can have $A$ values as low as $10^{-19}$ at a resistance of 100 $\Omega$. Individual, isolated single wall carbon nanotubes (SWNT)$^{18}$ have $A$ values around $10^{-5}$. So simply from a device performance point of view, a single PEDOT nanowire is 100 ~ 1000 times less noisy than a single SWNT. However, Hooge’s empirical law states that $A$ is inversely proportional to the number of carriers in the system. Without charge carrier density information, it is difficult to do a normalized comparison. However, the measured $A$ values of around $10^{-7}$ for PEDOT nanowires qualitatively reflect quite a high degree of disorder. Further optimization to decrease noise, proposed in Section 3.2.1.3, is again justified here.
3.2.2.3 Temperature Dependence of Noise

The noise power at 1 Hz of five PEDOT/PSS nanowires was measured in vacuum and presented in a semi-logarithmic plot against temperature in the range of 300-380 K (Figure 3-8). Compared with the simulation shown in the graph, all of the samples appear to follow a thermally activated process with similar activation energy of about 0.28 eV.

Figure 3-7: Relative noise power for the PEDOT/PSS and PEDOT/ClO₄ nanowires in the air.
A detailed discussion about the likely physical origin of 1/f noise in conducting polymers is outside the scope of this chapter. Temperature dependence data in a broader temperature range is needed and appropriate models need to be found in future work in order to shed some light on the noise generating mechanisms.

### 3.2.2.4 Effect of the Atmosphere on Noise

Figure 3-9 shows that the noise level of a typical PEDOT/PSS nanowire is a few times larger in air ( ~ 25% relative humidity) than in vacuum. Similar behavior was also observed for PEDOT/ClO$_4$ nanowires. Noise in nitrogen is only slightly, if at all, larger than in vacuum. This is probably caused by the moisture in the air. Polar water molecules
are absorbed into the polymer, modulate the noise generating mechanism and add to the noise level. It is interesting to notice that noise is far more sensitive than average resistance to the atmosphere change. The room air (25% relative humidity) increases the resistance by only a few percent (data not shown) while increasing noise by a few times. So we agree with the proposal of Bruschi\(^{45}\) that flicker noise could be utilized as a signal in gas/vapor sensing. Combined with simple resistance monitoring, better sensor performance might be achieved.

![Figure 3-9: Effect of the atmosphere on the noise of a PEDOT/PSS nanowire.](image)

3.3 Experimental

The multi-segmented Au-PEDOT-Au nanowires were synthesized using anodic aluminum oxide (AAO) membranes (Anodisc 25 with 0.2 µm pore diameter from
Whatman). A thin layer of Ag was first evaporated onto one side of the AAO membrane to serve as the working electrode. The first Au segment was then deposited galvanostatically at 0.65 mA/cm² current density using a commercial Au plating solution (Orotemp 24 from Technic Inc.). The PEDOT/PSS sample was deposited in a solution of 0.05M 3,4-ethylenedioxythiophene and 0.1M poly(styrenesulfonic acid) (PSS) in 1:1 water/acetonitrile at a constant potential of 1.0V. The PEDOT/ClO₄ sample was polymerized from a solution of 0.01M EDOT, 0.1M lithium perchlorate in acetonitrile at 1.4V vs. a Ag/AgCl electrode. The second Au segment was grown using electroless deposition⁴⁶ and then elongated by electrodeposition galvanostatically at 0.65 mA/cm² current density. For electroless deposition, the membrane was successively immersed into 0.025 M SnCl₂ and 0.07 M trifluoroacetic acid in 50:50 methanol/water (3 minutes), 0.03 M AgNO₃ in 0.3 M aqueous ammonia (2 minutes), and a solution containing 0.008 M Na₃Au(SO₃)₂/0.129 M Na₂SO₃/0.625 M HCHO adjusted to pH 5-6 (over 12-24 hours). After each solution, the membrane was rinsed thoroughly with DI water. The membrane was dissolved in either 5M HClO₄ solution (24 hours at 40 °C) or 0.5M NaOH solution (room temperature for half an hour) and then rinsed in methanol and isopropanol for at least three times each.

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. Optical images were obtained with a Zeiss Axiotech microscope equipped with a Sony DFW-X700 camera. FE-SEM images were obtained with a JEOL JSM 6700L field emission scanning microscope. TEM images were obtained with a JEOL 1200 EXII at 80 kV accelerating voltage.
For the noise measurements, the current from the sample was measured with the low-noise current preamplifier SR570. The device has an option to apply DC bias voltage to drive a current through the wire. It also has an offset current option to prevent input overload, so one can use high gain. The base noise level with both the bias voltage and the offset current was checked by measuring standard resistors of comparable values. It was found that the base noise level is much lower than the noise from the nanowires and is of the order of the input current noise of the preamplifier itself. The output voltage from the current preamplifier was digitized using a lock-in amplifier (SR830) by connecting the output from the signal preamplifier to the built-in analog-to-digital transform option. We also used the lock-in noise measurement option to verify our experimental procedure and the data from both methods were in an agreement. The noise power density was determined by averaging 100 periodograms of the current signal taken at the rate 512 Hz during a time interval 10 seconds. To decrease the effect of “aliasing”, i.e. an artificial increase of the measured power spectral density due to the presence of signal with finite amplitude with the frequency above the Nyquist frequency, we used a 12 dB low pass filter with 1 kHz bandwidth. In addition, we made a correction to the averaged periodogram by extrapolating the $1/f$ dependence to higher frequencies and decreased the power spectral density by the value of their expected input. All the noise measurements were carried out in a two-point system.
3.4 Conclusions

In conclusion, multi-segmented Au-PEDOT-Au nanowires synthesized in alumina membranes were assembled into a four-point test structure and characterized individually. The electrical transport properties of the PEDOT/PSS nanowires were found to be on the insulating side of the M-I transition and dominated by a hopping mechanism. In contrast, the PEDOT/ClO₄ nanowires were slightly on the metallic side of the M-I transition. The vapor sensing results of the two types of sensors were compared and different sensing mechanisms were proposed based on the transport data. Water and methanol increases the resistivity of the PEDOT/PSS nanowires and decreases the resistivity of the PEDOT/ClO₄ nanowires. The response of the PEDOT/PSS may be due to an increase of the hopping distance or decreasing of the hopping rate in the conducting polymer, while that of the PEDOT/ClO₄ is possibly through partial charge transfer between the polymer and the adsorbed vapor molecules.

A preliminary study on the electrical noise of both types of nanowires was carried out within the linear regime of conduction. The measured noise spectral densities follow a 1/f frequency dependence for both samples. The noise coefficient of PEDOT/ClO₄ nanowires is an order of magnitude smaller than that of PEDOT/PSS nanowires. The noise magnitude in air is a few times larger than that in vacuum for both types of nanowires. Noise increases with temperature in the temperature range of 300-380K.

The noise problem is more prominent in nanoscale devices than in macroscopic samples since Hooge’s empirical law states that A is inversely proportional to the number of carriers in the system. When the device scales down, the number of charge carriers...
decreases and the noise usually becomes larger. With the rapid growth of research in nanoscale electronic device components, it is timely to take the noise study to a deeper level. Dr. Alexey E. Kovalev will continue the effort in this direction.

3.5 References


Chapter 4

The Morphology of Template-Grown Polyaniline Nanowires and its Effect on the Electrochemical Capacitance of Nanowire Arrays

4.1 Introduction

Intrinsically conducting polymers are useful materials in sensors, electroluminescent devices, polymer-based electronics, and organic photovoltaic cells, because they are electronically conducting or semiconducting while retaining the mechanical, processing and cost advantages of polymers.\textsuperscript{1} In order to exploit nanostructural effects in these devices, several methods have been developed for fabricating conducting polymers as thin films, nanospheres, nanowires, nanotubes, and core-shell structures.\textsuperscript{2,3} Among these, the hard template method\textsuperscript{4,6} is especially useful for making conducting nanowires and nanotubes of controllable dimensions. Resistors, diodes and field-effect-transistors based on conducting polymer nanowires have been demonstrated.\textsuperscript{4,5} Fast electrochromic devices based on poly(3,4-ethylenedioxythiophene) (PEDOT) nanotubes have recently been described.\textsuperscript{6,7} We have recently studied conducting polymer nanorods grown by the hard template method as sensors for solution-phase and gaseous analytes.\textsuperscript{11-13}

Polyaniline is a particularly interesting conducting polymer because of its stability under in air and water, high conductivity in its oxidized/protonated form, acid-base properties, electrochromic behavior, and electrochemical capacitance.\textsuperscript{8} Polyaniline has been used in sensors and biosensors,\textsuperscript{15-18} solar cells,\textsuperscript{9} batteries,\textsuperscript{10} electrochromic devices,\textsuperscript{11}...
and antistatic coatings. Because of its high specific capacitance, polyaniline is also one of the most promising materials for electrochemical supercapacitors.

The porosity and internal structure of conducting polymer nanowires and nanotubes play a crucial role in their properties and device performance. However, the means of controlling their morphology without the use of templates are so far rather limited. Huang and Kaner developed rapid-mixing and interfacial polymerization methods to make polyaniline nanofibers chemically. Liu and coworkers devised a three-step electrochemical route to polyaniline nanowires. However, nanotubes, nanofibers, and nanowires made by these methods are either interconnected or non-uniform. This chapter describes a systematic study of the electrochemical growth of polyaniline from aqueous H₂SO₄ solutions in anodic aluminum oxide (AAO) membranes, and the effect of different parameters on the morphology of the resulting nanowires. The Galvanostatic charge-discharge method was used to measure the electrochemical capacitance of arrays of polyaniline nanowires, which correlates well with their morphology. Current transient data for nanowire growth can be interpreted quantitatively in terms of instantaneous and progressive nucleation and growth models, and this analysis is consistent with the observed concentration and potential dependence of nanowire vs. nanotube growth.
4.2 Results and Discussion

4.2.1 Synthetic Control of PANI Nanowire Morphology and the Mechanism Study

4.2.1.1 Effect of Electrolyte Concentration

We observed that H$_2$SO$_4$ concentration strongly affects the morphology of the resulting polyaniline nanowires. Figure 4-1 shows optical microscope images in cross-section of alumina membranes containing the nanowires, and TEM images of typical wires released from the membranes. In the optical images, the gold-colored band is the evaporated and electroplated gold that functions as the working electrode contact. The dark band above the gold is the polymer contained in the parallel cylindrical pores. Nanowires grown in 0.25 M H$_2$SO$_4$ solution are typically dense. The TEM image (Figure 4-1c) of such a wire shows a predominantly solid cylinder with a tubular morphology and thinning tube walls near the growth end. In contrast, the nanowire (Figure 4-1d) grown in 1.5 M H$_2$SO$_4$ solution appears tubular (from the light contrast in the center of the cylinder) for most of the length of the wire.
Conducting polymer morphology depends on nucleation and growth processes. Therefore in order to understand the morphology observed under different synthetic conditions, it is necessary to study the nucleation and growth mechanism. Current transients of polymerization are commonly used to probe the nucleation and growth mechanisms of conducting polymers. Figure 4-2 shows current transients from a series of experiments in which the H₂SO₄ concentration was varied from 0.25 M to 3 M. The inset shows the current transient at 0.25 M H₂SO₄ concentration on a longer time scale. All the I-t curves follow the same trend. There is an initial current drop, which is typical of polyaniline electropolymerization. It has been attributed in different studies to charging current, oxidative electroadsorption of monomers, and substrate passivation. Following the initial current drop, the current rises slowly to a maximum value before gradually falling again.
The current maximum can be analyzed by comparing the I-t data with theoretical plots for different modes of polyaniline nucleation and growth. The theoretical I-t characteristics for 3-dimensional instantaneous nucleation (3DIN) and 3-dimensional progressive nucleation (3DPN) under diffusion control are given by Equation 4.1 and Equation 4.2, respectively:36-38

\[
\frac{I^2}{I_m^2} = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2 \quad \text{Equation 4.1}
\]

\[
\frac{I^2}{I_m^2} = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367(t/t_m)^2]\}^2 \quad \text{Equation 4.2}
\]

Figure 4-3 compares dimensionless current-time plots, obtained from the experimental data in Figure 4-2 with theoretical curves for progressive and instantaneous 3D nucleation process under the diffusion control. At low H\textsubscript{2}SO\textsubscript{4} concentration, very good agreement between the experimental data and the theoretical plot for progressive
nucleation under diffusion control is obtained. At higher H₂SO₄ concentrations, the experimental data fall in the region between progressive and instantaneous nucleation, which are two extreme cases of the nanowire growth mechanism.

![Figure 4-3: Dimensionless plots of I-t behavior, comparing data from Figure 4-2 with theoretical curves for 3-dimensional progressive and instantaneous nucleation under diffusion control.](image)

The 3-d nucleation model suggests that in the early stage of polymerization, the current increases as a result of the increase of the number of nuclei and their size. The growth rate is controlled by hemispherical diffusion to the nuclei. At a certain point, the growth rate reaches saturation as hemispherical diffusion gives way to linear diffusion. The current then decreases as the monomer concentration near the electrode decreases.

Referring again to Figure 4-2, the current maximum shifts to a shorter time and higher current as the H₂SO₄ concentration increases. This can be explained by a faster diffusion rate of monomers to the electrode at higher H₂SO₄ concentration. The increase
of diffusion coefficient with increasing electrolyte concentration has been observed in other systems,\textsuperscript{18, 19} and is possibly due to the modulation of the hydrodynamic radius of the diffusing species as the ionic strength changes.\textsuperscript{20}

Another effect of increased H\textsubscript{2}SO\textsubscript{4} concentration is the increased rate of hydrolysis of the polyaniline,\textsuperscript{21} which is an important reason for the increased porosity of the nanowires. There is thus a trade-off between the porosity and the stability of the polyaniline nanowires. At 0.1 M aniline concentration, when the H\textsubscript{2}SO\textsubscript{4} concentration is over 2 M, the synthesized nanowires are not stable and lose their electrochemical activity after several charge-discharge cycles in the potential window of 0 to 0.7 V vs. SCE.

### 4.2.1.2 Effect of Polymerization Potential

Figure 4-4 shows the transition from porous to dense nanowires as the potential of polymerization is made less anodic. In these experiments, the monomer concentration was kept at 0.1 M and the H\textsubscript{2}SO\textsubscript{4} concentration was kept at 2 M, i.e. under similar conditions that gave a mixture of progressive and instantaneous 3D nucleation at a potential of 900 mV in Figure 4-3.
Figure 4-4: TEM and optical images of polyaniline nanowires synthesized at different potentials.

Figure 4-5: Current transients of polyaniline synthesized at different potentials.
In order to understand the mechanism of nucleation and growth, we again recorded current transients during polymerization (Figure 4-5). At 900 mV, as expected, the I-t curve follows the diffusion-limited 3-d nucleation and growth model. However, at potentials lower than 800 mV, a completely different behavior was observed. The current increases exponentially with a shoulder at an early stage of the reaction. The exponential current increase is consistent with 1-dimensional chain branching\textsuperscript{22, 23}. However, no specific morphology has been clearly connected to this kind of growth in the literature. Therefore, we studied the morphology of nanowires grown under 1-d chain branching conditions. The body of the nanowire always appears dense under the optical microscope. What is interesting is that many of the nanowires have saw-tooth ends, which suggests that the nanowires are actually bundles of interconnected nanofibers that are 30-80 nm in diameter (Figure 4-6a, b). This observation is consistent with the hypothesis of Kaner\textsuperscript{24} that polyaniline possesses an intrinsic morphology of nanofibers. Indeed, we observed some free nanofibers (Figure 4-6 c, d) in the nanowire suspension.
In comparison, 3-d nucleation under diffusion control usually gives nanowires with a tubular end of decreasing wall thickness at low H$_2$SO$_4$ concentration. In this case, no nanofibers are found in the suspensions. The top end of the tube becomes very thin and in some cases breaks off as thin flakes. A typical example is shown in Figure 4-7a. The total length of these nanowires is about 20 micrometers. More than 75% of the growth end of the wire is tubular with decreasing wall thickness towards the end. Figure 4-7b illustrates the tubular morphology and the different wall thickness at different points along the tube. As the initially tubular nanowires grow with time, both the length and the proportion of the dense part increase. In contrast, when the H$_2$SO$_4$ concentration is high, the nanowires remain porous throughout their growth.

**Figure 4-6**: TEM images of samples synthesized under 1-d chain branching growth. Saw-tooth ends of nanowires (a, b). Some loose nanofibers in the nanowire suspension (c, d). The sample in a and b was grown in a solution of 0.1 M aniline and 2 M H$_2$SO$_4$ at 750 mV. The sample in c and d was grown in a solution of 0.2 M aniline and 2 M H$_2$SO$_4$ at 800 mV.
4.2.1.3 Effect of Monomer Concentration

The applicability of the diffusion-controlled mechanism should also depend on the monomer concentration, since Fick’s first law states that the diffusion flux is proportional to the concentration gradient.\textsuperscript{25} Indeed, we observed a transition in the current transient behavior at high monomer concentration, as shown in Figure 4-8. At 0.1
M aniline concentration, the I-t transient has the shape expected for 3D nucleation and growth under diffusion control. At 0.5 M, there is a current maximum followed by continuous current increase, reminiscent of the behavior observed at lower overpotential in Figure 4-5. Under these conditions, the growth appears to follow a combined 3-d and 1-d mechanism. TEM images showed that the nanowires become denser with increasing monomer concentration, consistent with this hypothesis.

4.2.2 Electrochemical Capacitance of PANI Nanowire Arrays

The galvanostatic charge-discharge method is a reliable way to characterize the electrochemical capacitance of materials under controlled current conditions. This measurement is relevant to the use of conducting polymers in different morphologies as components of supercapacitors. Figure 4-9 shows the charge-discharge curves of a typical polyaniline nanowire array at three different charge-discharge rates. The measurements were done in 1 M sulfuric acid with the polyaniline nanowire arrays inside the AAO membranes.
The specific capacitance \((C_s)\) was evaluated via equation 
\[ C_s = \frac{I}{m \cdot \frac{dV}{dt}}, \]
where \(I\) is the discharge current, \(m\) is the total mass of the polyaniline nanowires in the array, \(\frac{dV}{dt}\) can be obtained from the slope of the discharge curve. The results on several different samples are shown in Table 1. In order to understand the effect of the nanowire array configuration, we also synthesized polyaniline films on gold-covered glass slides for comparison. The specific capacitance of nanowire arrays appears to be higher than that of films made under the same conditions. This is exemplified by sample 1 and sample 2. The specific capacitance of the array structure (sample 2) is about 20% more than that of the film (sample 1). This is easy to understand since the nanowire array structure improves the accessibility of electrolytes as a result of the partial etching of AAO membrane in the electrolyte. The specific capacitance of the arrays can be further increased by complete removal of the AAO membrane (data not shown).

**Figure 4-9:** Galvanostatic charge-discharge curves of a polyaniline nanowire array synthesized in a solution of 0.1 M aniline and 1.5 M H\(_2\)SO\(_4\) at 900 mV.
Comparing sample 2 and sample 3, one can see the effect of the electrolyte concentration on specific capacitance. As discussed above, higher H₂SO₄ concentration

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Polymerization Conditions</th>
<th>Mass of polyaniline (mg)</th>
<th>$C_s$ at a discharging rate of 1A/g (F/g)</th>
<th>$C_s$ at a discharging rate of 2.5A/g (F/g)</th>
<th>$C_s$ at a discharging rate of 5A/g (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Film)</td>
<td>0.5 M aniline, 0.5 M H₂SO₄, 900 mV</td>
<td>2.4</td>
<td>440</td>
<td>430</td>
<td>400</td>
</tr>
<tr>
<td>2 (Array)</td>
<td>0.5 M aniline, 0.5 M H₂SO₄, 900 mV</td>
<td>3.3</td>
<td>520</td>
<td>500</td>
<td>480</td>
</tr>
<tr>
<td>3 (Array)</td>
<td>0.5 M aniline, 2 M H₂SO₄, 900 mV</td>
<td>1.6</td>
<td>760</td>
<td>730</td>
<td>710</td>
</tr>
<tr>
<td>4 (Array)</td>
<td>0.1 M aniline, 0.25 M H₂SO₄, 900 mV</td>
<td>2.0</td>
<td>550</td>
<td>520</td>
<td>480</td>
</tr>
<tr>
<td>5 (Array)</td>
<td>0.1 M aniline, 1.5 M H₂SO₄, 900 mV</td>
<td>0.77</td>
<td>780</td>
<td>700</td>
<td>610</td>
</tr>
<tr>
<td>6 (Array)</td>
<td>0.2 M aniline, 2 M H₂SO₄, 800 mV</td>
<td>1.6</td>
<td>410</td>
<td>370</td>
<td>340</td>
</tr>
<tr>
<td>7 (Array)</td>
<td>0.2 M aniline, 2 M H₂SO₄, 900 mV</td>
<td>1.4</td>
<td>540</td>
<td>460</td>
<td>430</td>
</tr>
</tbody>
</table>
induces a more open morphology. Consequently, sample 3, which was made in 2 M H$_2$SO$_4$, has higher specific capacitance than sample 2, which was made in 0.5 M H$_2$SO$_4$. A similar trend was seen in sample 4 and sample 5. When the H$_2$SO$_4$ concentration increased from 0.25 M to 1.5 M, the specific capacitance of the array also increased.

The effect of polymerization potential on specific capacitance is illustrated by sample 6 and sample 7. Sample 6 was made at 800 mV and has a dense morphology. Sample 7 was synthesized at 900 mV and shows some porosity under TEM. This leads to higher specific capacitance in sample 7.

The monomer concentration effect is somewhat surprising. Comparing sample 3 and sample 7, the higher monomer concentration in sample 3 led to a sample of slightly denser morphology than sample 7. However, the specific capacitance of sample 3 is actually higher. This can be attributed to the poor integrity of sample 7 caused by hydrolysis, which was confirmed by the observation of broken polyaniline pieces in TEM images. Monomer concentration is another important factor in determining the degree of hydrolysis because of the competitive reaction between aniline and water with the polaronic hydrolysis precursor. Thus, sample 3, which was made in a solution of high aniline concentration, has good sample integrity even at high H$_2$SO$_4$ concentrations.

Sample 3 has a specific capacitance of 710 F/g at a discharging rate of 5 A/g. This is close to the highest reported value of polyaniline capacitance to the best of our knowledge, approximately 768 F/g, at similar discharging rates. Further optimization may be possible by fine-tuning of the synthetic conditions or by using other strategies. For example, it has been demonstrated that conducting polymer composite nanowires with metal oxides of high specific capacitance exhibit improved supercapacitor
Selective removal of the inorganic phase in conducting polymer composite nanowires is an effective way to introduce extra porosity into the nanowires.

The energy density of these nanowire arrays, on a mass basis, is above the US Department of Energy goal (over 15 Wh/kg energy density at a power density of at least 1.5 kW/kg). Using sample 3 in Table 1 as an example, at 1.75 kW/kg power density, the energy density is approximately 50 Wh/kg. The energy density was calculated from \( E_s = E/m \), and \( E = \int Vdt \), where \( E \) is the energy and \( \int Vdt \) can be obtained from the area under the galvanostatic discharge curve. The power density \( P_s \) can be calculated from \( P_s = P/m \), and \( P = dE/dt \). However, the thickness of the commercial alumina membranes is limited to 60 micrometers. Thus, the amount of polyaniline in an electrode prepared in this manner is limited to a few milligrams per cm\(^2\). Thus, the total power and energy is very limited. From application point of view, it remains to be seen if polyaniline nanowire arrays with similar porosity can be grown on higher surface area electrode structures, either by growing hard templates conformally on the electrode or by using soft template methods.

### 4.3 Experimental

Aniline, sulfuric acid, gold plating solution (Orotemp 24), and gold etchant (GE-8148) were purchased from Aldrich Chemical Co., EMD, Technic Inc., and Transene Company Inc., respectively. AAO membranes (Anodisc 25 with 0.2 µm pore diameter) were purchased from Whatman. Dialysis tubing with 12,000-14,000 molecular weight cut-off was obtained from the Spectrum Chemical and Laboratory Products.
Light microscopy was carried out with an Olympus BX60M reflected-light microscope equipped with an Olympus U-CMAN-2 camera (Olympus, Japan). Transmission electron microscopy (TEM) images were obtained with a JEOL 1200 EXII at 80 kV accelerating voltage. Electrochemical experiments were performed using either a BAS 100B or a EG&G/Princeton Applied Research model 363 potentiostat/galvanostat in a one-compartment, three-electrode cell at room temperature. A BAS LG-50 galvanostat was used to perform the constant current charge-discharge characterization. The reference electrode was a saturated calomel electrode (SCE). All potential values are reported versus the SCE. A Pt coil was used as the counter electrode.

A layer of gold about 110 nm thick was deposited onto the branched side of the AAO membranes using a BOC Edwards FL400/Auto306 thermal evaporator. This gold film was used as the working electrode contact for further electroplating of gold and polymerization of aniline in the pores. A gold layer a few micrometers thick was electroplated galvanostatically at 0.65 mA/cm$^2$ current density before the aniline polymerization step. Polymerization was done at constant potential in aqueous solutions of aniline and sulfuric acid under varying conditions of concentration. TEM samples were prepared by dissolving the gold back of the membrane in the gold etchant followed by dissolving the membrane in 5 M H$_2$SO$_4$ at 40°C for 20 hours. The nanowires were then purified by dialysis against Millipore nanopure water or methanol for 2 days.

The mass of the polyaniline nanowire array was measured by using the following procedure. The AAO membrane was rinsed thoroughly with water, dried under flowing nitrogen and stored in a vacuum desiccator for several hours. The weight was then measured on a Sartorius BP211D balance to an accuracy of 0.01 mg. After polyaniline
deposition, the membrane was rinsed, dried and weighed in the same way. Since the alumina membranes slowly dissolve in the H$_2$SO$_4$-based polymerization solution, the weight of the polyaniline nanowires has to be compensated by the alumina weight loss. The polymerization solution was therefore collected after the reaction, and the aluminum concentration in the solution was measured on a Leeman Labs PS3000UV inductively coupled plasma spectrophotometer and converted to alumina weight loss of the membrane.

4.4 Conclusions

The electrochemical synthesis of polyaniline nanowires in aqueous H$_2$SO$_4$ solutions was investigated. Increasing the H$_2$SO$_4$ concentration during growth induces a transition from solid nanowires with tubular ends to open nanowires. The nanowire morphology correlates with nucleation and growth mechanisms deduced from current-time transients. At high anodic potential (900 mV), the current transient data fit a 3-d diffusion-controlled nucleation and growth model. Depending on the H$_2$SO$_4$ concentration, the nanowires can exhibit a porous morphology or have a tubular growth end with decreasing wall thickness towards the tip. At lower anodic potential, the I-t curves fit a 1-d chain branching model. The resulting nanowires have a dense morphology and appear to consist of interconnected small fibers. The electrochemical capacitance of polyaniline nanowire arrays was characterized as a function of growth conditions. In general, open morphology and better sample integrity increase the specific capacitance.
4.5 References


Chapter 5

Composite Nanowires with Added Functionalities: Guided Autonomous Motion in Heterogeneous Magnetic Fields

5.1 Introduction

One of the biggest challenges in nanoscience is to create autonomously powered nanomechanical devices that mimic biological motor systems.\(^1\) Nature harnesses chemical potential energy to support motions crucial to physiological functions.\(^2, 3\) The elegance and precision of the control has amazed human beings and inspired physical scientists to follow. A few years ago, Paxton et al. provided the first example of autonomous artificial motors on the nano- or microscale.\(^4\) A simple gold-platinum (Au-Pt) bimetallic nanorod catalyzes the decomposition of hydrogen peroxide and powers its own motion in the liquid medium. The mechanism of this model system has ever since been under intense investigation.\(^5-7\) Now some other groups around the world have also started developing devices with similar functions.\(^8-10\)

Gaining the ability to designate the movement paths of artificial motors will demonstrate a higher level of control of this nanomachinery system and is relevant to a number of potential applications. Although the Au-Pt bimetallic nanorod system moves preferentially towards one end, the direction is subject to random fluctuation as a result of unavoidable thermally induced rotation. Kline et al. demonstrated a methodology to control the direction of the movement.\(^11\) By introducing nickel (Ni) segments into the Au-Pt nanorods, they created transversely magnetized nanorods and longitudinally
magnetized nanorods which could be “remote controlled” by a stack of magnets several centimeters away.

The Fischer group developed a system which has the potential to define the movement path of magnetic motors.\textsuperscript{12} The local magnetic field distribution was controlled by using the magnetic domains on an underlying garnet film substrate. The domains on the garnet film have magnetization vectors either up or down as is shown in the scheme in Figure 5-1 (perpendicular to the garnet film). Since the magnetic field is the strongest along the domain walls, magnetic colloidal particles in the liquid medium above the film can be attracted to the domain walls.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5-1.png}
\caption{Labyrinth created with garnet films. The top graph is a scheme of the system. The substrate contains domains with alternating up and down magnetization vectors. The magnetic particles in the water above this substrate tend to align along the domain walls. The bottom graph is an optical microscope image of a film. The deep grey and light grey regions represent the two domains. The colloidal particles are deposited forming a pattern along the domain walls after solvent evaporation.}
\end{figure}
The bottom graph in Figure 5-1 is an optical microscope image of the substrate with magnetic colloids aligned along the domain walls after evaporating the solvent. The formed pattern by the colloids does not change even after the magnetic field is altered or removed. Therefore this system originally provided an interesting way to assemble colloidal particles into patterns.

This system was also proposed as a network of tracks to guide the autonomous motors. The challenge then was to design and synthesize “shuttles” that align on the domain walls and autonomously move along the “rails”. The transversely magnetized nanorods with nickel segments mentioned above failed in this mission, (see Section 5.3 for details.) which puzzled us and led us to the question of what controls the dynamics and how to achieve track-directed motion.

We proposed to use superparamagnetic nanocrystals as one of the building materials to construct this “nanoshuttle”. When confined into a nanowire shaped space, the collective effect of all the nanocrystals should help align the anisotropic nanowire along the domain wall.

Conducting polymers were proposed as the host material for these superparamagnetic nanocrystals. Owing to their insolubility in most solvents, stability, easy synthesis, compatibility with many other materials and their “soft” and porous nature, conducting polymers prove to be an excellent matrix to accommodate nanoparticles and create composites. Hernandez initiated the work on conducting polymer composite nanowires in the Mallouk group.\(^6\)\(^{13}\) She developed methods to incorporate proteins, including avidin, streptavidin, and oxido reductase (catalase), into PPy nanowires and explored the possibility of using these composite nanowires for
biosensing. It is interesting to determine whether magnetic functionality could be added into conducting polymer composite system as well.

This chapter presents the development process of a “nanoshuttle” with PPy and superparamagnetic nanocrystals. Also included is mechanistic information on the interplay between propulsion and magnetic steering through the comparison of this composite nanowire with several other artificial and natural motors in heterogeneous magnetic fields.14

5.2 Synthesis of Polypyrrole-Magnetite Composite Nanowires

The original design of the “nanoshuttle” included four segments (Figure 5-2). This architecture included the Au-Pt core for its asymmetric catalytic function and two conducting polymer ends in order to align the anisotropic nanoparticle along the domain wall.

![Figure 5-2](image)

**Figure 5-2:** Scheme of the initial design of a nanowire structure for guided movement in heterogeneous magnetic fields. The blue ends represent conducting polymer segments with magnetite nanocrystals (shown as light blue dots, size not to scale).

Magnetite (Fe₃O₄) nanocrystals were chosen to provide magnetic functionality because of its well-known superparamagnetism. Negatively charged stabilizing agents were preferred since the $p$-type conducting polymers can possibly incorporate them better. The synthesis of magnetite nanocrystals were carried out using a published method¹⁵ of
FeCl$_2$ (anhydrous, Aldrich) and FeCl$_3$ (anhydrous Acros) (1:2 molar ratio) coprecipitation in ammonium hydroxide. Specifically, 2.822 g FeCl$_3$ and 1.097 g FeCl$_2$ were mixed in 80 mL of DI water in a three-necked flask, and bubbled with nitrogen for about 30 minutes to remove dissolved oxygen. Then the mixture was heated to 80 °C with continued nitrogen flow for protection from oxidation. While vigorously stirring the reaction mixture, 10 mL concentrated ammonium hydroxide was added drop by drop with a syringe within 10 minutes. After 30 minutes, 2 g citric acid monohydrate, which was dissolved in 4 mL of DI water, was added. The reaction temperature was increased to 95 °C and stirring continued for 2 hours.
The synthesized nanoparticles were then rinsed by centrifuging and re-suspending in DI water for several cycles. The final suspension was passed through a polycarbonate filter membrane (Nuclepore from Whatman) with 30 nm pore diameter to get rid of aggregates. Figure 5-3 shows TEM images of synthesized Fe$_3$O$_4$ nanocrystals. Freshly made samples have size in the range of 4-20 nm, mostly distributed around 10 nm. Storage in the aqueous suspension leads to slow increase of particle diameter. Roughly speaking, the diameter increased by a factor of two in 10 days. Samples stored for more than two weeks cannot be effectively incorporated into the polymer system described in

**Figure 5-3**: TEM images of synthesized magnetite nanocrystals.
the following paragraph, possibly due to a change in the surface citric layer or simply as a result of the increased particle size.

A few problems during the synthesis of the target P-Au-Pt-P (P stands for polymer magnetite composite) nanowire structure will be addressed next as well as solutions to them. The first problem was the base metal. We started with palladium (Pd) or silver (Ag) deposition, planning to use that segment as the working electrode for polymer composite deposition and then the further deposition of Au, Pt and polymer composite in order to obtain the designed structure shown in Figure 5-1. After synthesis, the Pd or Ag layer can be easily and selectively removed by acid etching. However, it was found that neither PPy nor the PPy/magnetite composite could be deposited on Pd/Ag. The reason was rather trivial. The anodic dissolution of these metals occurs at the potentials needed for electropolymerization of Py. After 10 minutes at 750 mV vs. SCE, the oxidation is visible on the back of the membrane. So a short segment Au, which has a higher oxidation potential, needs to be deposited on top of the Ag sacrificial layer to minimize the accessibility of electrolyte solution to the Ag electrode and provide a stable substrate for the PPy nucleation and growth.

The optimized conditions for PPy/magnetite composite electrodeposition is: constant potential growth at 750 mV vs. SCE from an aqueous solution of 0.1M Py, 0.05M citric acid as a supporting electrolyte/dopant and magnetite nanocrystals. Magnetite is trapped into PPy during electropolymerization possibly due to the electrostatic interaction between the positively charged polaronic PPy chains and the citric acid stabilized negatively charge nanocrystals, the coordination between iron and
pyrrole/PPy nitrogen and other forces. Figure 5-4 shows the PPy segment loaded with magnetite nanocrystals.

![TEM image of a PPy magnetite composite nanowire segment.](image)

**Figure 5-4**: TEM image of a PPy magnetite composite nanowire segment.

The second problem encountered was that Au cannot be electrodeposited on top of a PPy/citric acid composite segment. This is illustrated in Figure 5-5. From the bottom of the membrane, a sacrificial silver segment, a small gold segment as nucleation site and a polymer composite segment were deposited in that sequence. Then Au electrodeposition was attempted using various electrochemical conditions. No growth could be achieved. In contrast, Pt was able to deposit on the polymer composite possibly because of the less negative reduction potential needed for the Pt plating. Many attempts to grow Au on top of this Pt layer also failed even after elongated plating time and careful adjustment of electroplating conditions. Figure 5-5 shows the result. One can see the Au-
P-Pt-P structure. However, the electrodeposition of Au anywhere above the polymer segment yielded nothing. Referring back to Section 2.2.1, the dedoping of conducting polymers possibly caused the leakage problem in those cases, while in the case of PPy/citric acid, it simply prevents electrodeposition of Au from happening. The electrochemical dedoping of conducting polymers changes their electrochemical and electrical activities and therefore interferes with the subsequent deposition steps. We were able to perform electroless deposition of Au on top of the polymer composite segment using the procedure described in the Experimental Section in Chapter 3. However, it is a time-consuming and tedious procedure.

Eventually, a “sequence altered” deposition strategy was developed as a simple and excellent solution to both problems. The process is the following. Four segments Ag, Au, Pt, PPy composite were electrodeposited in sequence in an AAO membrane. Then Ag was electrodeposited on top of the PPy composite until it grew out of the 60 micrometer thick membrane to form a continuous layer. The electrochemical cell was

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**Figure 5-5:** One of the failed attempts to grow Au-P-Au-Pt-P nanowires (optical microscope image). No Au deposited directly or indirectly on top of a PPy/citric acid magnetite composite segment.
then disassembled. The Ag originally evaporated onto the back of the AAO membrane and the Ag segment that was first deposited were dissolved in nitric acid. This releases free space on one side of the membrane again. The overgrown long silver originally on the top was then used as the bottom working electrode for deposition. A segment of PPy composite was electrodeposited into the void space in the pore, which was released from nitric acid etching of Ag mentioned above. In short, instead of growing the nanowire in the normal sequential fashion, we altered the deposition sequence of the segments.

Figure 5-6: Optical microscope images P–Au–Pt–P nanowires as originally designed synthesized using an “sequence altered” deposition strategy.

Figure 5-6 shows the nanowires obtained with the “sequence altered” deposition method. This strategy conveniently circumvents the two problems described above. No direct deposition of polymer on top of Ag/Pd is needed. No Au deposition on top of PPy
is involved either. It might be of general interest to the synthesis of other types of multi-segmented nanowires too, especially when compatibility issues between the different segments come into play.

Surprisingly, the designed structure, P-Au-Pt-P, does not move autonomously towards one end in 3-7% hydrogen peroxide as we expected. Its movement in hydrogen peroxide is more like Brownian motion. To diagnose this, P-Au-Pt nanowires and Au-Pt-P nanowires were synthesized. The former does not preferentially move towards either end, while the latter moves towards the polymer composite end effectively. An explanation of this behavior is that magnetite is a catalyst for the decomposition of hydrogen peroxide. The propulsion from the polymer magnetite ends competes with or adds to the propulsion from the Pt segments. This explained the behavior of all samples. We therefore simplified our design and synthesized the Au-P sample shown in Figure 5-7.
Figure 5-8 shows superconducting quantum interference device (SQUID) magnetometry measurements results (Quantum Design MPMS 7T) of Au-P rods (bottom) and Au rods (top) as a control. The Au control is diamagnetic. For the Au-P nanowires, the magnetic moment continues to increase with the applied field, which indicates paramagnetism. There is no hysteresis. So the possibility of ferromagnetism can be excluded.

Figure 5-7: TEM images of Au-PPy magnetite composite nanowires.
The Au-P nanowires have two functionalities that result from the embedded magnetite nanocrystals: magnetic steering and catalytic propulsion. Since the polymer composite end has an aspect ratio (length/diameter) of about 6, its orientation on the garnet film should be along the domain walls. The following section will discuss measurements in the heterogeneous magnetic field, which were performed by our collaborators in Fischer’s group. The text below is mostly excerpted from a collaboration paper.\textsuperscript{14}

Figure 5-8: SQUID measurement results. Magnetic moment versus the magnetic field for Au nanowires (top) and Au-PPy magnetite composite nanowires (bottom).
5.3 Autonomous Movement of Various Motors in Heterogeneous Magnetic Fields: Guided Motion versus Roving

Several samples with different magnetic and propelling properties were studied on the garnet films in order to gain some insight into the controlling factors of the motion in the heterogeneous magnetic field. Figure 5-9 shows the scheme of heterogeneous magnetic field system with a garnet film as the substrate and the samples investigated. “Type P” refers to the Au-P nanowire sample described above. “Bacteria” is Magnetotacticum gryphiswaldense, a ferromagnetic natural motor. “Type FT” is transversally magnetized ferromagnetic nanorods with Pt and Au segments for propulsion and oblate nickel (Ni) segments. “FL” refers to longitudinally magnetized nanorods with Au and Pt as well as prolate Ni segments. “+” and “−” mean their magnetization directions are the same and the opposite of the direction of the movement, respectively. Various motors and their behavior in the heterogeneous field will be discussed one by one.
Magnetic and propulsion energies of the various motors above the garnet film were estimated. Magnetic energies were calculated as \( E = \mu_0 m M_s \), \( \mu_0 \) the permeability of vacuum, \( M_s \) the magnetization of the garnet film (\( M_s = 11 \text{ kA/m} \)). The magnetic moment \( m \) is the permanent ferromagnetic moment for the ferromagnetic navigators and the induced paramagnetic moment is taken from the SQUID measurement in Figure 5-8 at a field of \( H=M_s \). The propulsion energy is obtained by measuring the power \( P = f \eta l v^2 \) with \( f \approx 20 \) the friction coefficient of the navigator, \( \eta \) the viscosity of water, \( l \) the length of the navigator and \( v \) its velocity outside a magnetic field. \( \gamma = v/l \) is the shear rate. As will be demonstrated later, the magnitude of these energies and their interplay are very important to the motion.

Figure 5-9: Scheme of a magnetic garnet film with upward (white) and downward (grey) magnetized domains forming a labyrinth pattern. Autonomously moving navigators, i.e. magnetotactic bacteria, paramagnetic or ferromagnetic rods of type P, FT, FL+ and FL− are placed in an aqueous solution above the garnet film, where they autonomously move.
Magnetotacticum gryphiswaldense. Magnetotacticum gryphiswaldense (Figure 5-10) are bacteria of length ~ 6.5 μm, and diameter ~ 0.7 μm, which contain membrane encapsulated vesicles (magnetosomes) filled with 40-100 nanometer Fe₃O₄ particles. The vesicles are aligned along the long axis of the bacterium. The magnetic moment of the bacteria is of the order $m \sim 1.5 \times 10^{-15} \text{ Am}^2$. The bacterium is propelled forward by flagella with a typical power (estimated from velocity) of $P \sim 10^4 \text{ kBTs}^{-1}$. In nature, their magnetic encompass and their oxygen concentration dependent motion helps them finding their favored environment.

<table>
<thead>
<tr>
<th>Type</th>
<th>$E_m/k_B T$</th>
<th>$P/\gamma k_B T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetotactic Bacteria</td>
<td>$4.6 \times 10^3$</td>
<td>$5.5 \times 10^3$</td>
</tr>
<tr>
<td>Type P</td>
<td>$5.7 \times 10^3$</td>
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</tr>
<tr>
<td>Type FT</td>
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<tr>
<td>Type FL</td>
<td>98</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5-1: Magnetic and propulsion energies of the motors above the garnet film.

1. Magnetotacticum gryphiswaldense. Magnetotacticum gryphiswaldense (Figure 5-10) are bacteria of length ~ 6.5 μm, and diameter ~ 0.7 μm, which contain membrane encapsulated vesicles (magnetosomes) filled with 40-100 nanometer Fe₃O₄ particles. The vesicles are aligned along the long axis of the bacterium. The magnetic moment of the bacteria is of the order $m \sim 1.5 \times 10^{-15} \text{ Am}^2$. The bacterium is propelled forward by flagella with a typical power (estimated from velocity) of $P \sim 10^4 \text{ kBTs}^{-1}$. In nature, their magnetic encompass and their oxygen concentration dependent motion helps them finding their favored environment.
Most of the bacteria are trapped on the domain walls. There is vigorous motion induced by the flagella; however, the field of the domain wall is too strong to let the bacterium escape. Therefore its motion is confined to the domain wall. Only very occasionally, a bacterium can escape the domain wall. Figure 5-11 shows an ensemble of bacteria trapped at the domain walls. A time sequence of the position of one bacterium, marked in color, is overlaid on an image of the garnet film.

The main reason bacteria do not function well as “nanoshuttles” is the orientation. The size of the magnetite particles (40-100 nm) in these bacteria determined that they are ferromagnetic. The orientation of the bacteria in the heterogeneous field is decided by the fact that the magnetite particles align along the long axis of the bacteria. Thus the bacteria long axis is perpendicular to the domain wall to align with the magnetic field lines. This

Figure 5-10: TEM images of a magnetotactic bacterium. The magnetite particles align along the long axis of the bacterium.
orientation is unfavorable for the “nanoshuttle” since it is perpendicular to the desired pathway defined by the domain walls.

2. Ferromagnetic rods. Transversally and longitudinally magnetized ferromagnetic nanorods (type FT and type FL nanorods) of diameter $2r=400$ nm and length $l=2.6 \mu m$ ($l=2.5 \mu m$) are subdivided into segments consisting of platinum $l_{Pt}=468$ nm ($l_{Pt}=356$ nm) followed by nickel $l_{Ni,1}=64$ nm ($l_{Ni,1}=311$ nm), gold $l_{Au,1}=957$ nm ($l_{Au,1}=533$ nm) and nickel $l_{Ni,2}=106$ nm ($l_{Ni,2}=444$ nm) and finally gold $l_{Au,2}=1.021 \mu m$ ($l_{Au,2}=889$ nm) (Figure 5-11). The two nickel segments of the rod are ferromagnetic. Their size is chosen small enough to ensure that the nickel has a single ferromagnetic domain, but large enough to suppress any superparamagnetic behavior. The type FT rods have an oblate geometry of the nickel segments ($l_{Ni}<<r$) and hence they favor the alignment of the nickel magnetization perpendicular to the rod (transversal

**Figure 5-11**: Polarization microscope image of magnetotacticum gryphilswaldiense (bright) on a magnetic garnet film. A time sequence ($t=0.9s$) of the tangential motion of one bacterium (colored) along a domain wall is shown.
magnetization). The type FL rods have prolate Ni segments with a magnetization pointing along the long axis. We use NdFeB magnets with a magnetic induction of 0.48 T to magnetize the rods (longitudinal magnetization). The magnetization of the nickel segments is \( M = 310 \text{ A/m} \) as estimated from the rod alignment in water in a magnetic field of \( H = 1 \text{ kA/m} \). This magnetization is about one percent of the bulk-nickel magnetization making their magnetic moment about one percent of the magnetic moment of the magnetotactic bacteria. Previous experiments showed that the type FT (type FL) rods once magnetized, align with their long axis perpendicular (parallel) to a magnetic field.

The type FL rods were observed to be randomly distributed above the garnet film. Table 1 shows that the magnetic energy is smaller than the propulsion energy. As a result, the FL rods are dominated by the autonomous motion. No steering with the heterogeneous magnetic field was achieved.

The transversely magnetized nanowires are especially interesting in this case, since their magnetic moment is perpendicular to the catalytically powered movement direction. This is favorable in terms of orienting the long axis of the rods along the domain walls. However, Figure 5-12 shows a typical trajectory of an autonomously moving type FT nanorod above the surface. Although the magnetic energy of the rod exceeds the thermal energy, the propulsion energy dominates the motion and their trajectory follows a statistical fractal path frequently crossing the stripes showing little correlation to the garnet structure. In principle, one can propose to increase the magnetic energy of the rods by increasing the number of Ni segments with oblate geometry in one nanowire. However, this is a synthesis challenge since when the number of layers increases, it is difficult to maintain the oblate geometry of the Ni segments.
3. Paramagnetic Au-PPy magnetite composite rods. Figure 5-13 shows a typical trajectory of an autonomously moving type P nanorod above the surface. Their magnetic moment in a field corresponding to the saturation magnetization $M_s$ of the garnet film is about the same as for the magnetotactic bacteria and the domain walls are again strong enough to trap most of the rods above the domain walls. However since the direction of the magnetic moment is not fixed the rods minimize their magnetic energy by placing all Fe$_3$O$_4$ nanoparticles directly above the domain wall where there is the strongest field. This lets the rods orient parallel to the domain wall. Their motion is purely one dimensional with the rods traveling along the path dictated by the domain walls. Hence the strategy to get a higher fraction of navigators travel along the path by using paramagnetic instead of ferromagnetic rods works well. Basically all of the rods are guided by the garnet structure.

Figure 5-12: SEM images of FT and FL nanowires (left). Polarization microscopy image of type FT nanowires (bright orange) on a magnetic garnet film. A typical fractal trajectory (white) of a nanowire is overlayed on the image.
From the experimental results above, one can have a better understanding of controlling factors of the nanoparticles’ motion in the heterogeneous magnetic field. The lesson we learned from the behavior of the bacteria motors is that ferromagnetic orientation is somehow in conflict with the desired propulsion direction. The magnetic field orients the majority of bacteria perpendicular to the stripe pattern, while one would like to guide them along the stripes/domain walls. In this sense, paramagnetic nanowires instead of ferromagnetic rods are favored, since the nanocrystals will always establish a magnetic moment in the direction of the magnetic field leaving the navigators more options to move in various directions. Alternatively one might try to achieve a synergy between the rod motion and magnetism by orienting the magnetic compasses perpendicular to the long axis such that the long axis lies along the domain wall of the garnet film and the magnetic moment points parallel to the magnetic field of the domain.

Figure 5-13: Overlay of polarization microscope images of a type P rod (yellow) on a magnetic garnet film. A time sequence (Δt = 2.8 s) of the motion along a domain wall of one rod (t = 0-16.8 s) is shown.
wall, a strategy that was followed by using the type FT rods. However, despite some preference of these FT rods for the domain walls, the propulsion overcomes the magnetic constraints.

5.4 Conclusions

A new artificial motor based on the conducting polymer composite nanowire structure has been designed and synthesized. Through the study of the behaviors of this and several other motors in a heterogeneous magnetic field, it was found out that the controlling factors for the motion include: (1) the orientation of the motors which is determined by the magnetic properties as well as the shape of the object. Longitudinally ferromagnetic rods take an orientation with their long axis perpendicular to the domain walls. This disfavored in the guided motion along the domain walls. While paramagnetic nanowires with high aspect ratio tend to align along the domain walls. (2) Synergy between propulsion and attraction to the “rails”. Transversely magnetized rods do not have enough magnetic energy to confine their motion to a certain magnetic potential plane. Thus their distribution is more or less random in the heterogeneous magnetic field.

Au-conducting polymer magnetite composite nanowires have the desired orientation, balanced magnetic energy and propulsion power. Therefore they move along the predefined path autonomously. In short, one should be able to control the guided motion vs. roving through adjusting the magnetic and propulsion energies while keeping both above thermal energy level. This is one tiny step closer to the nanomechanical devices that can deliver interesting cargo to a designated target in a guided way.
5.5 References


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Publications

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