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14. ABSTRACT
This project involves a novel approach to the synthesis of new classes of materials designed to function as ion conducting systems. In particular, we are developing new methods to produce materials with new chemical characteristics which can be used to modulated electrical behavior on the nanoscale. The current phase of this proposed work is designed to identify promising candidates and to study the mechanism by which ions are transported though these new solids. The ulitmate goal is to produce a working lithium battery incorporating new electrolytes.

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Program Title: Bioinspired Routes to Lithium-Ion Conducting Polymers and Nanomembranes

Principal Investigator: John Arnold, University of California, Berkeley.

Agreement Number: FA9550-1-0066

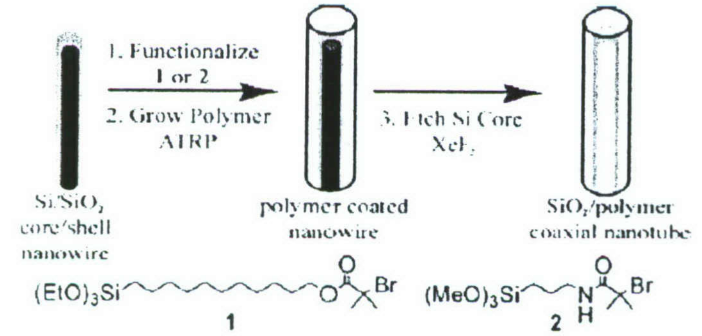
Objectives

This project involves a novel approach to the synthesis of new classes of materials designed to function as ion conducting systems. In particular, we are developing new methods to produce materials with new chemical characteristics which can be used to modulated electrical behavior on the nanoscale. The current phase of this proposed work is designed to identify promising candidates and to study the mechanism by which ions are transported through these new solids. The ultimate goal is to produce a working lithium battery incorporating the new electrolytes.

New Materials from Surface Initiated Atom Transfer Radial Polymerization (ATRP) on Inorganic Nanowires.

There currently exists an interest in nanostructured materials for varied applications including biotechnology,[1,2] battery technology, and sensing technology, each of which demand different chemical and physical properties. The realization of these devices will be dependent on the ability to modify and assemble nanoscale building blocks. Surface initiated polymerization promises to be an important tool to further develop the chemical and physical properties of nanostrutures, by providing a method to covalently attach polymer chains in a well-controlled fashion. Such modifications could tailor important properties such as wetting and aggregation of the nanostructures. With application of this technique to the inner surface of inorganic columnar materials, devices with high ionic conductivities could be achieved. During the past year we developed a method for obtaining a multifunctional material using procedures based on ATRP by growing polymers directly on silicon/silica core/shell nanowires. The template wires from these inorganic-organic hybrid structures can then be etched away to leave nanotubes which are open at one end and closed at the other. As a result of our synthetic procedure these nanotubes will have different functionality on the inner and outer surfaces presenting a hydrophobic outer wall with a hydrophilic inner surface (scheme 1).

Scheme 1



The synthesis of silicon nanowire arrays was carried out using published procedures. Residual gold catalyst was removed by successive HF and KI/I_2 etching. A silica layer was then formed by thermally oxidizing the array under a flow of oxygen at 850 °C for 1-8 h. By varying the oxidation time silica layers with different thicknesses can be obtained, thus providing a route to many silica tubes with variable diameters. In order to initiate a polymerization from the surface of the wires they were functionalized with initiator molecules **1** and **2.** ATRP is then catalyzed by a copper complex in the presence of methyl methacrylate, glycidyl methacrylate, and ethyleneglycol dimethacrylate as monomers for the polymerization. These silicon/silica/polymer structures have been characterized extensively using Electron Microscopy, Electron Energy Loss Spectroscopy, Energy Dispersive Spectroscopy, and Raman Spectroscopy. The resulting polymers have been characterized using Gel Permeation Chromatography and Refractive Index measurements. Subsequent removal of the silicon from the core using a mild XeF_2 etch, results in nanotubes with hydrophobic polymer shells and a hydrophilic silica inner surface. The chemistry developed making these materials is being extended to other inorganic nanostructures and will developed further to make functional materials which can be used to study single tube ion conduction.

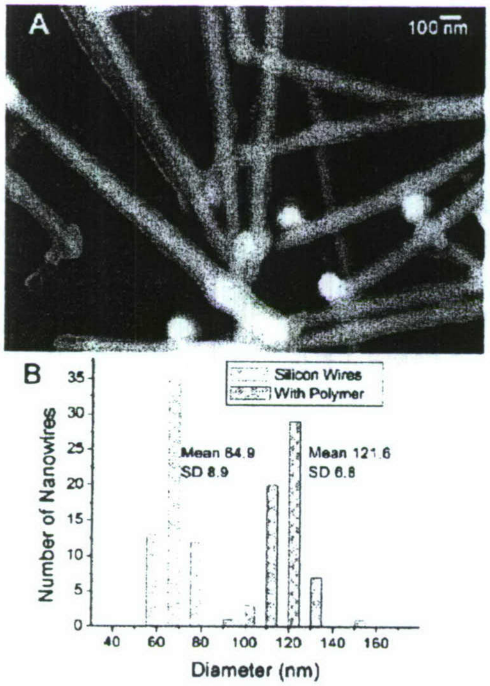


Figure 1. (A) SEM micrograph of silicon nanowires coated with PMMA (B) Histogram of starting wire thickness compared with the thickness after polymerization. On average, the polymer thickness is 28 nm

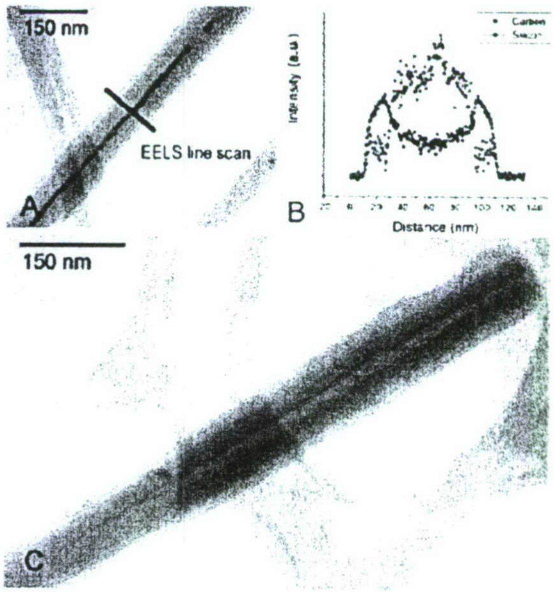


Figure 2. (A) TEM micrograph showing the modification of silicon/silica core/shell nanowires with PMMA. (B) Electron Energy Loss Spectrum taken using the nanoprobe scanning mode in a Philips CM200 TEM, showing the relative amounts of carbon and silicon present in the polymer-coated nanowire. (C) TEM micrograph of the resulting polymer-coated nanotubes after etching with XeF_2

In addition to the work completed on silicon wires, similar chemistry has been worked out for ZnO nanowires. Wurzite ZnO nanowires have drawn much attention as building blocks for incorporation into devices because of their semiconductor, optical, and mechanical properties. Work in this arena has focused on the synthesis and material properties ZnO nanostuctures, and because of this a wide array of materials are available. ZnO is also an ideal template material because it can be produced in large quantities with defined geometries and can then be easily dissolved by exposure to mildly acidic conditions. This reality has allowed us to characterize the extent of the polymerization more completely including an analysis of the polymer produced and experiments to quantify the number of initiator groups on the surface (Figures 4a and b). Using ZnO as a template, the polymers grown by ATRP have been shown to serve as precursors for carbon tubes via pyrolysis. These carbon tubes are orders of magnitude larger than typical carbon nanotubes and are shown to be comprised of graphitic and amorphous domains. These tubes are the first carbon based hollow nanostructures on this size scale and could find application as electrode materials, catalyst supports, or as a chemically modifiable sheath for other 1D nanostructures.[3]

By varying the ligand on the CuBr and the reaction conditions, polymerizations of methyl methacrylate, glycidyl methacrylate, phenyl methacrylate, ethylene glycol dimetharylate, styrene, and acrylonitrile were all successful preformed. For the methyl methacrylate polymerization the time and conversion dependant polymer characteristics where studied using GPC and refractive index measurements (figure 4a). We have shown that by controlling the time of polymerization, along with the amount and type of monomers added both the thickness and the properties of the polymer can be tailored. In particular we have shown polymer thicknesses ranging from 5–15 nm (figure 4b), with the upper bounds being dependant on the inner wire spacing. A wide range of homopolymers were grown from the surface as were block co-polymers. The ability to reinitiate and grow block co-polymers demonstrates that this is a well controlled polymerization and that this method could be extended toward the isolation many more polymer types.

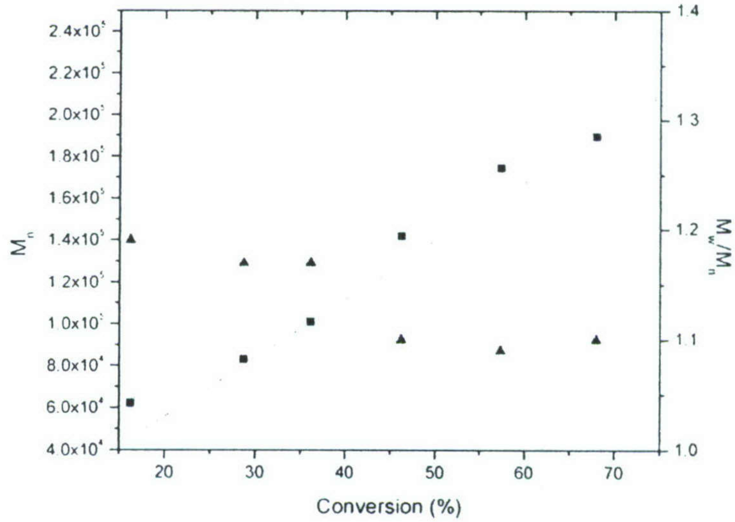


Figure 4 a) The depenance of Mn on percent converion is shown by the squares and follows very close to the predicted trend shown as the dashed line. The triangles show the PDI as a function of percent conversion which decreases slightly as is expected for ATRP.

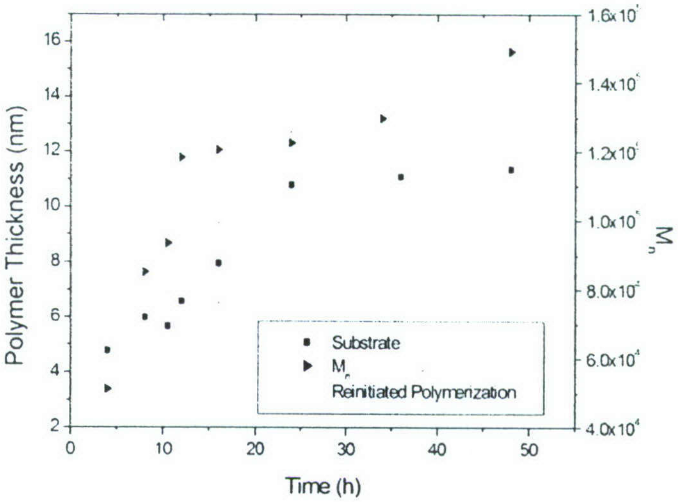


Figure 4 b) The change in polymer thickness as a function of time is shown as squares and can be seen to increase with time. As expected the Mn of the polymer follows the same trend as the thickness (represented by triangles).

Carbon tubes were prepared from ZnO nanowires coated with various polymers. Both traditional templating routes using polyacrylonitrile (PAN) dissolved in DMSO dip coated onto ZnO arrays, and arrays coated with polymer via surface initiated ATRP were examined. Each method produces arrays of carbon nanotubes with one end closed. The dip coating route produces nanotubes with thicker walls but less ordered structures based on Raman spectroscopy; while the substrates prepared from surface initiated polymerization produced much thinner walled carbon tubes with a more intense peak corresponding to graphitic ordering. The degree of ordering in graphitic structures may be determined by comparing the intensities of the G band (E_{2g} mode) and D band (disordered band) peaks in the Raman spectrum. For single crystalline graphite only one peak at ~1575 should be observed; all other graphitic material including carbon nanotubes also show the D band at ~1355 (Figure5).

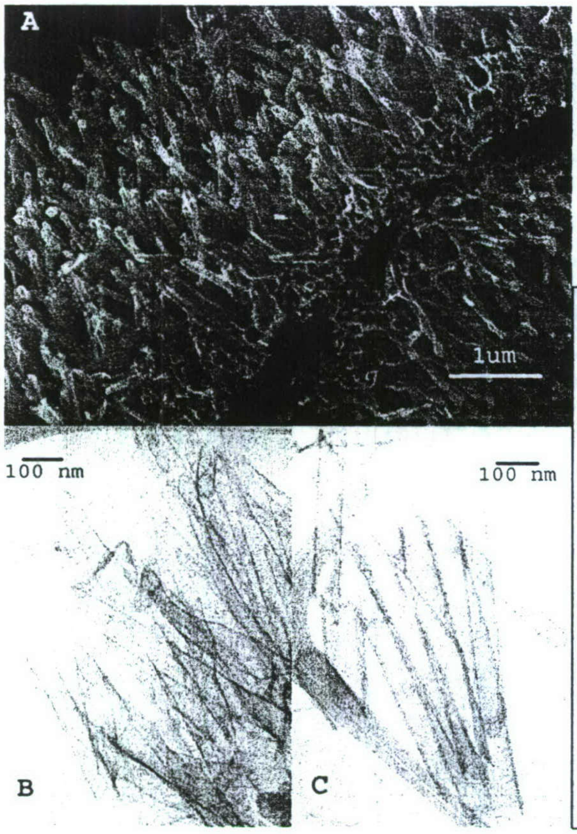
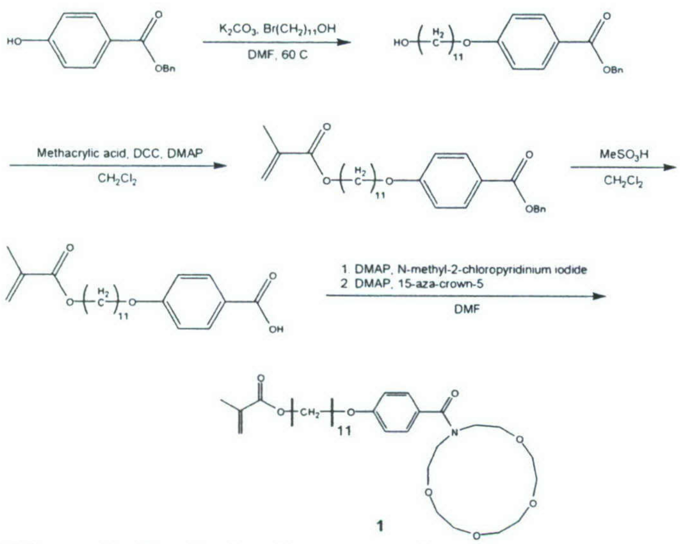


Figure 5 a) SEM of Pyrolysis product from a surface initiated polymerization of PMMA on ZnO. b) TEM micrograph of the sample in (a). c) TEM micrograph of the pyrolysis product from a dip coated PAN on ZnO. d) Raman spectrograph showing the intensities of the ordered and disordered bands of graphite from each of the method of preparation.

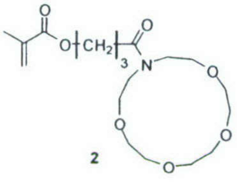
Crown-ether polymers.

We previously reported on a new crown-ether containing polymer for lithium ion conduction. The particular crown used, an amide linked aza-crown, was chosen based on our work on liquid crystalline materials which showed a high lithium ion exchange rate in NMR experiments. Based on this observation monomer 1 was synthesized as summarized in scheme 2.



Scheme 2. Synthesis of monomer **1**.

This work has continued with the synthesis of three more monomers to which will enable us to elucidate structure/function relationships.



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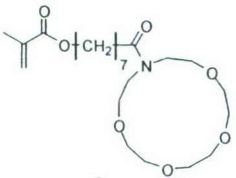

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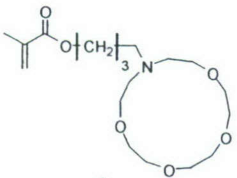

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The first of a series of aza-crown containing polymers have been synthesized by free radical polymerization of **1**, and Li-ion conductivities of several lithium to repeat unit ratios measured by AC-impedance. Ratios of 1.5:1, 1:1 and 0.5:1 Li:repeat were investigated and conductivities of 10^{-8} to 10^{-5} S/cm were found between 35° and 100° C, with the 1.5:1 ratio having the best conductivity followed closely by the 0.5:1 ratio. The synthesis of the next generation of monomers, lacking the aromatic unit, has been carried out and awaits polymerization and AC-impedance measurements. The monomers which will be investigated, **2-4**, should have higher conductivity due to their greater flexibility which should lead to lower glass transition temperatures. This series will give us valuable information about the effects of varying chain length and the presence of an amine vs. an amide.

Personnel Supported

Mr. Craig Reeder, 5th year graduate student, 50% time
Mr. Ben Rupert, 5th year graduate student, 100% time
Mr. Martin Mulvihill, 2nd year graduate student, 100% time

Publications

Mulvihill, M. J.; Rupert, B. L.; He, R. R.; Hochbaum, A.; Arnold, J.; Yang, P. D. Journal of the American Chemical Society 2005, 127, 16040-16041.

Rupert, B.R.; Mulvihill, M.J.; Arnold, J. "Atom Transfer Radical Polymerization on Zinc Oxide Nanowires" Chem. Mater. 2006, 18, 5045 - 5051

Rong Fan, Seong Huh, Ruoxue Yan1, John Arnold, Peidong Yang "Gated Proton Transport in Mesoporous Silica Films".. Nature Mater. 2008, 7, 303-307

John

John Arnold, May 18, 2008

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