**Nanoreactor Processes for Manufacturing Oriented Materials**

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PIs: Seong H. Kim, Henry C. Foley, Stephen J. Fonash, Ayusman Sen, Paul S. Weiss
Pennsylvania State University, University Park, PA 16802

The goal of this project is to develop new nanomanufacturing approaches that utilize carefully designed nanoscale reactor/assembler systems to align and assemble oriented nanomaterials as they are produced, rather than trying to manipulate them afterwards. The use of templates for nano-wire and nano-filament creation has received a great deal of attention. The common approach based on nano-templates is to use the templates strictly for growth and then etch or dissolve them to release the produced nano-wires. These nano-wires must then be “caught” and directed to their point of use. In this process, the big challenge that must be overcome for mass production of nanowire-based electronics and sensors is that one must be able to align and assemble these nanowires by design, not by statistics. Once nano-wires are released from the template, it is very difficult to obtain spatial and orientational control in nanowire assembly as well as electrical contacts at a specific location. In order to circumvent this problem, we are developing new nanomanufacturing processes that utilize nanofabrication techniques (a) to create nano-devices in which growth of functional materials completes the final electrical contacts and interconnects or (b) to construct chemical reactors that can constantly produce and transfer oriented nanomaterials onto a substrate in a controlled way, mimicking a spider weaving a spider web. Our approach will enable “just-in-place” synthesis of nanomaterials.

We have developed the full process flow for producing these nanochannel templates with controlled dimensions, spacing, orientation, and built-in electrical contacts. Our templates are fabricated by the combined use of electron-beam lithography, a sacrificial metal line etching technique, and adequate direct etching technique like reactive ion etching. The entire processing is fully convertible to more high-throughput type processing approach such as the step and flash lithography. A completed nano-channel template with four built-in contacts and two reservoirs is seen in Figure 1. These electrodes can be used for either electrochemical reactions or for serving as the final contacts for completed arrays. The reservoirs allow precursor entry into the templates.

Synthesis of conducting polymers inside these nanochannels with built-in electrodes can produce electronic devices or sensors. We have synthesized polypyrrole inside the nanochannels in two ways: (a) FeCl$_3$-catalyzed oxidative polymerization by introducing FeCl$_3$ solution from one side of the nanochannel and pyrrole monomer from the other side and (b) electrochemical polymerization inside nanochannels using built-in electrodes. Figure 2 shows the current-voltage
are currently under investigation.

nanowires of consisting reactor result outside shows AAO nanochannels. to catalyst activated surface a anodized Ziegler-Natta production processes.\[1\]

Nano-filaments shows carried polymerization parent gas. exposing the impregnating polynorbornene, channel initiator produced as production calculated to be 2.5 S/cm. conductivity being measurement data of five polypyrrole nanowires together, each being 200nm wide, 60nm thick, and 100\[m\] long. The conductivity of these electrochemically produced nanowires is calculated to be 2.5 S/cm.

Our nanochannel reactor approach can be applied to production of a number of different polymers. Polymers such as poly(methyl methacrylate), poly(acrylic acid), etc. can be produced by filling the channels with a solution containing an initiator dissolved in monomer liquid followed by heating the channel to polymerization temperature. Polymers such as polynorbornene, polyacetylene, etc. can be produced by impregnating catalysts inside the channels and then exposing them to monomer gas. Since the capping layer of the nanochannels is UV transparent silicon nitride, photo-polymerization can also be carried out easily. Figure 3 shows examples of polymer nano-filaments produced by these different polymerization processes.[1]

In order to test the possibility of continuous production and extrusion of polymeric nanowires from the nanochannels, we are studying the Ziegler-Natta polymerization of ethylene using anodized aluminum oxide (AAO) membranes as a model reactor. TiCl\(_4\) is chemisorbed on the surface OH group of the AAO channels and activated by reactions with Al(C\(_2\)H\(_3\))\(_3\). The catalyst loaded AAO channels are then exposed to C\(_2\)H\(_4\) gas for polymerization inside the nanochannels. The cross-sectional view of the AAO channels after polymerization (Figure 4) shows that some polyethylene fibers are produced outside the channels, which might be the direct result of polymerization extrusion from the channels. This polymerization process will be incorporated with a high-pressure membrane flow reactor to facilitate extrusion of the produced polymers. In this reactor, one side of the membrane consisting of arrays of nanochannels is charged with high-pressure monomers and the other side of the membrane is pulled by vacuum in order to use pressure gradient to push the polymeric nanowires while they are produced inside nanochannels. More details and process optimization are currently under investigation.
Incorporation of a nanoporous membrane through which monomer diffusion is allowed, but not polymers, can enhance the control of monomer supply polymer extrusion direction. The nanoporous carbon (NPC) synthesis inside nanochannels has been accomplished via pyrolysis of polyfurfuryl alcohol mixed with a surfactant inside the channels (Figure 5). The process developed here is also suitable for production of nano-turfs of NPC fibers of a diameter of 40 ~ 100nm and a length from a few microns to hundreds microns. The nano-turfs of NPC provide high external surface area to volume ratios that will be useful in a range of applications including as membranes, catalytic media, sensor elements and high performance adsorbents with low mass transfer resistance. Transport rates into and through such materials will benefit dramatically from the nanoscale diffusion lengths.

We also have studied continuous production of polymeric nanofibers via a jet-blowing process in collaboration with Prof. J. Badding in the Penn State Chemistry Department. Polymer is loaded in a heated reservoir behind a micro-nozzle and high pressure (7500 ~ 30000 psi) is applied across the nozzle. A shear force induced by extremely fast flow of gas stream through the nozzle draws polymer fibers from the loaded polymer surface and elongation of these fibers occurs while they pass through the nozzle along with the carrier gas. This process enables fiber production of non-melt processible polymers such as Teflon (Figure 6). The produced fibers are 150nm to a few microns in diameter and tens to hundreds micrometers long.

A significant effort has been made to make broader impacts. The advances made in this project have been disseminated through the Penn State Nanofabrication Facility user base. The project poster is displayed at the Facility, one of the four “full service” sites of the NSF National Nanofabrication Users Network (NNUN) which is utilized by over 200 non-Penn State users and about 100 Penn State users annually. The project outcomes are often incorporated in a number of outreach programs operated by the Facility including the Nanofabrication Manufacturing Technology (NMT) Partnership, the Nanofab’s NSF ATE Center for Manufacturing Education, three-day professional development workshops for secondary school educators as well as industry personnel, and “chip camps” for middle school and high school students from across Pennsylvania. Kim and Sen organized a session at the 226th ACS National Meeting focusing on polymer-inorganic interfaces and nano-templated polymer syntheses to stimulate more research in this area. One REU student from Longwood University, VA, has been trained with NSF support in 2002 summer.

References: