Creating unique polymeric particles

Two different methods of making polymeric particles from two different teams result in quite similar particles. Each group has fabricated custom designed polymeric particles with complex geometric shapes, going from spherical to unique nonspherical shapes, enabling a variety of new technologies in diverse areas such as photonics, diagnostics, and functional materials.

Using common lab chemicals and equipment

A method that uses routine lab chemicals and equipment to make polymeric particles in more than 20 different shapes and features in reproducible quantities ranging from 60-nm dia to 30-µm dia has been demonstrated by researchers at the Univ. of California, Santa Barbara (UCSB). This method offers independent control over particle properties like size and shape using spherical particles to create nonspherical particles. Generally, in the process, polystyrene (PS) particles from two different teams result in quite similar particles. Each group has fabricated custom designed polymeric particles with complex geometric shapes, going from spherical to unique nonspherical shapes, enabling a variety of new technologies in diverse areas such as photonics, diagnostics, and functional materials.

A) Less complex shapes are made by liquefication followed by stretching and solidifying a film. B) More complex shapes are made by first stretching the film, then liquefying and solidifying. C) Unique shapes are created by combining the two methods. Source: Proceedings of the National Academy of Sciences

The last method combines these processes to create unique shapes such as ribbon-like particles with curled ends or porous elliptical disks.

UCSB, www.ucsb.edu

Microfluidics + projection photolithography

A high-throughput and high-resolution microfluidic method that synthesizes polymeric particles has been developed by researchers at the Massachusetts Institute of Technology (MIT), Cambridge. Called stop-flow lithography (SFL), this method uses compressed air-driven flows rather than syringe pumps to synthesize the particles. Also, this method synthesizes particles using materials that cannot be easily spin-coated, enabling the use of a wider range of materials.

Generally, in the three-step stop-flow lithography method, a flowing stream of oligomer is driven through a microfluidic channel using a pressure profile provided by a computer controlled three-way solenoid valve that alternates between atmospheric pressure (closed) and a specified input pressure (open).

In the first step, the flow is stopped by closing the three-way valve. In the second step, an array of particles is polymerized into a stationary monomer film using ultraviolet (UV) light by opening a shutter for 0.05 sec while keeping the three-way valve closed. In the final step, polymerized particles are flushed out of the channel by opening the three-way valve while keeping the shutter closed. These steps are repeated with as many as 300 exposure cycles/min by rapidly cycling through the stages of stop-polymerize-flow. Particles are then flowed out into a large reservoir where they are developed and collected.

The microfluidic device is fabricated by pouring polydimethylsiloxane on a Si wafer that contains positive-relief microchannels patterned in SU-8 photosresist. Four different microchannel heights (2-µm, 10-µm, 20-µm, and 40-µm tall) are tested with a constant width of 200 µm and a length of 1 cm. As channel height decreases, the system slows down due to the increased resistance to flow that must be overcome to squeeze fluid out of the microchannel.

MIT, www.mit.edu

CNT demand soars

The global carbon nanotube (CNT) market is projected to exceed $1.9 billion by 2010, according to the report “Carbon Nanotubes: A Global Strategic Business Report,” by Global Industry Analysts Inc., San Jose, Calif. Currently, the U.S. dominates the world market in terms of revenue. By 2010, the European CNT market is projected to be the fastest growing market at a compound annual growth rate (CAGR) of over 100%. During this same time frame, the U.S. and Asia-Pacific will account for 75% of the global CNT market with the Asia-Pacific region reaching $2.5 billion by the year 2012. The multi-walled carbon nanotube (MWNT) market was estimated at $290 million for 2006. However, in the coming years, the single-walled carbon nanotube (SWNT) market is projected to overtake the MWNT market by the year 2012 with revenues of $5 billion and a CAGR of 200%.

Global Industry Analysts Inc., www.strategyr.com

New surface plasmon

An acoustic surface plasmon, a new type of electron wave that exists on metal surfaces, has been proven to exist by Bogdan Diaconescu and Karsten Pohl, Univ. of New Hampshire, Durham. The acoustic plasmon can be excited with any wavelength. These plasmons have been predicted on theoretical grounds, and last year, a team concluded that they did not exist. This work proves their existence. Because this new mode with its acoustic dispersion allows light to be contained on small surface areas and in a broad frequency range, it has implications for research in nano-optics and photonics applications.

Univ. of New Hampshire, www.unh.edu

NANOTECH BRIEFS
Nanotechnology

Nanotubes behave like supercompressible springs

Long, vertically aligned multiwalled carbon nanotubes (MWNTs) under repeated high compressive strains that display viscoelastic behavior similar to soft-tissue membranes have been reported by Pulickel Ajayan at Rensselaer Polytechnic Institute (RPI), Troy, N.Y. A large-area block composed of MWNTs is compressed and released at a strain of 15% over half a million cycles. Under compressive cyclic loading, the mechanical response of the MWNTs shows preconditioning (stress-softening) behavior, viscoelasticity-induced hysteresis, nonlinear elasticity and stress relaxation, and large deformations. Also, at 15% strain level, MWNT shrinkage is below the 10% fatigue damage (shrinkage) limit—less than 5% shrinkage along the MWNTs’ height is observed.

Due to the multifunctional properties of MWNTs, their electrical properties are simultaneously measured when the mechanical compression and release is carried out. The MWNTs still retain their electrical properties.

Potential applications are in synthetic biopolymers, electromechanical sensors, and contact brushes. RPI, www.rpi.edu

Process Measurement and Nanotechnology

Blown-bubble nanofilms from bubbles

Blown-bubble nanofilms that consist of dense, uniformly aligned nanowires or nanotubes over a large area have been demonstrated by Charles Lieber at Harvard Univ., Cambridge, Mass. The film is created using a version of the blown film extrusion method, a manufacturing process that is used to make products like garbage bags and food packaging.

The method has three key steps in creating bubble-blown films (BBFs). In the first step, a polymer suspension of homogenous and stable Si nanowires or nanotubes is prepared. As an example, the nanowires are modified using 5,6-epoxyhexyltriethoxysilane and are combined with an epoxy solution.

Then, the polymer suspension is transferred to a die (55-mm dia) and forms a membrane covering a gas outlet at the bottom of the die. Then the flow of nitrogen (N2) gas begins to expand the membrane forming a bubble—bubbles are formed with diameters >25 cm and heights >50 cm. A ring at the die’s center traps the bubble’s top surface area and directs its vertical expansion at a constant speed. Due to the upward thrust, the height between two steel plates with four holes at each corner and subjected to large compression cyclic strain for 500,000 cycles. All cycles are performed at a test frequency of 0.75 Hz. After 500,000 cycles, the block retains its original structure with a slight reduction along the length of the MWNTs. The mechanical stress–strain curve shows a viscoelastic behavior.

Due to the multifunctional properties of MWNTs, their electrical properties are simultaneously measured when the mechanical compression and release is carried out. The MWNTs still retain their electrical properties.

Potential applications are in synthetic biopolymers, electromechanical sensors, and contact brushes. RPI, www.rpi.edu

NANOTECH BRIEFS

AC Josephson effect detects mechanical motion

The AC Josephson effect that can be used to detect mechanical motion of atoms or nanostructures has been reported by Alexei Marchenkov and Uzi Landman, Georgia Institute of Technology (Georgia Tech), Atlanta.

In the work, a niobium (Nb) dimer nanowire acts as a weak link between two superconducting (bulk) Nb electrodes in a microfabricated junction. The team hypothesizes that the new measured peaks likely originate from mechanical motion of the dimer, which causes enhancement of the electrical current at particular values of an applied voltage. At each of the peak voltages, the frequency of the AC Josephson current resonates with the vibrational frequency of the nanostucture in the junction.

Georgia Tech, www.gatech.edu

Nanosoccer debuts

The first nanoscale soccer games at the 2007 RoboCup in Atlanta were hosted by the National Institute of Standards and Technology (NIST), Boulder, Colo., on July 7-8. In the competition, soccer nanobots were operated under an optical microscope, were controlled by remote electronics using visual feedback, and were seen on a monitor with real-time viewing of the soccer playing field (1.5-mm across with a 900-µm x 500-µm goal on either side) and the soccer ball (microdisk; ~50-µm dia).

Called nanobots due to their mass, which ranged from a few nanograms to a few hundred nanograms, they were tens of micrometers to a few hundred micrometers long. To win the competition, a nanobot must be fast, agile, and capable of manipulating objects tested in three events. The overall winner was the ETH Zurich team from Switzerland.

NIST, www.nist.gov
Manipulating and visualizing samples concurrently

A form of subwavelength microscopy consisting of an electrode-free, continuously tunable, coherent visible light source that uses individual potassium niobate (KNbO₃) nanowires has been demonstrated by Jan Liphardt at the Univ. of California, Berkeley, and Peidong Yang at the Lawrence Berkeley National Laboratory, Calif. This single KNbO₃ nanowire optically traps, doubles the frequency of a trapping light, and waveguides the locally generated light to its ends, providing a form of scanning transmission mode and fluorescence mode, all in one instrument.

Generally, in the work, KNbO₃ nanowires (50-nm dia) are synthesized in a hot water solution with the growth axis orthogonal to the pump beam and then separated using ultrasound. Then, the KNbO₃ nanowires are optically trapped using infrared (IR) optical tweezers with a trap wavelength at 1,064 nm. Here, the nanowires spontaneously orient to the optical axis of the trap/pump laser. This results in a detectable second harmonic generation (SHG) signal along the growth axis. By varying the wavelength of the pumping laser, the color that the nanowire emits also changes.

To test the device, the IR laser trap holds the nanowire in position while a pattern of gold (Au) ridges (200-nm wide, 50-nm thick with decreasing pitch between each ridge) is scanned. Each time the nanowire passes over an Au pitch, there is a reduction of transmitted SHG. By measuring the light transmitted through the sample, the spacing of the lines resolves to ~100 nm. This occurs due to the narrowness of the nanowire, which is smaller than the wavelength of the light that the nanowire emits.

In another test, a fluorescent polystyrene bead glows without exciting other beads due to the placement of the end of the nanowire against it. When the nanowire is removed, the fluorescence is reduced 80-fold. This indicates that the 532-nm SHG emitted by the nanowire is the predominant source of excitation.

Future work will focus on adapting and interpreting signal-processing and signal-deconvolution algorithms developed for AFM and NSOM to this nanowire scanning microscope. 

Univ. of California, Berkeley, www.berkeley.edu
Microfluidics to Change the World of Chemistry

The world is flat, some people say, but, happily, there are still cultural differences. This is a good thing for science, as there wouldn’t be many new discoveries with everybody heading in the same direction. When Columbus couldn’t convince the Portuguese that sailing to the West was an interesting project, he received ships from the Spanish king. Thanks to the Dutch climate of tolerance, many books about religion, philosophy, and science that were forbidden as being too controversial in other European countries were printed in the Netherlands.

Even today with the easy and rapid flow of scientific and technical information around the globe, we still see those cultural differences. Look at microfluidics for the chemical industry as an example. A significant interest was attracted in recent years for several reasons:

- For small quantities, chemists tend to use batch process, but often continuous processing is easier to control, while the residence time distribution and the heat transfer can be much better controlled.
- Scaling up is also much easier: instead of building it bigger, it just needs additional items of the same (tested) set-up.
- As a consequence, compared to traditional installations, microfluidics-based installations tend to be smaller, more energy efficient, safer, higher yielding, and easier to expand.

But let’s come back to cultural differences: enablingMNT did a survey of international activities in the area of microfluidics for the chemical industry—the following “culturally-induced” strategies were discovered:

- The German approach is based on their impressive work on LIGA and other micromachining technologies. With these technologies, they are able to build a wide variety of metal valves, pumps, reactor chambers, etc. Currently they are actively promoting the use of complete standardized systems (backbones) facilitating the construction of miniaturized chemical installations.
- The Japanese followed another route; their idea is that efficient use of microreactors is only possible using specifically designed chemical reactions. The consortium they have set up to study and promote microfluidics in the chemical industry is therefore dominated by chemical companies and is studying chemical processing in microreactors.
- In contrast, American and British companies are proposing chemical installations based on microchannels. Their installations are aiming to replace traditional chemical reactors and are constructed from steel. They are aiming to exploit the current interest in energy production and are making use of one of the most outstanding advantages of microfluidics: efficient heat transfer.
- The Dutch are also following a conservative route. They have introduced microreactors but are proposing to use the original chemical (batch) reactions.
- Keanu Zhang, co-editor of the latest enablingMNT report on MEMS activities in China, explained the Chinese approach: “China is a big country; there are many people in poor living conditions, so China is looking for technology breakthroughs to bring cheap and accurate healthcare to its citizens. Therefore, for us, the most interesting application area for microfluidics is in the overlap of chemistry and biology.”

There are as many views as there are cultures. One thing everybody agrees on is that we are only beginning to tap the wealth of possibilities of chemistry with microfluidics.

—Patric Salomon, 4M2C PATRIC SALOMON GmbH, Germany

—Henne van Heeren, EnablingM3, The Netherlands
Doughnut-shaped microcavities that detect single biomolecules in real time without labeling a target molecule with fluorescent tags have been developed by Kerry Vahala at the California Institute of Technology (Caltech), Pasadena. The optical sensor is based on an ultrahigh Q whispering gallery microcavity (microtoroid resonator). Its surface is functionalized to bind the target molecule in which the binding is detected via a resonant wavelength shift.

The Si microtoroid resonators are fabricated using a three-step process. First, oxide pads are lithographically defined. Then, a Si wafer is etched with xenon difluoride, which forms arrays of microdisks. Finally, these disks are reflowed with a laser. A tunable laser and detector are coupled to these microtoroids using an optical fiber waveguide.

The Si surfaces of the microtoroids are coated with biotin or antibodies to capture specific molecules. Then, the microtoroids are immersed in water or human blood serum containing the protein. Here, a laser light interacts with the molecules causing a binding interaction which creates red-shifts of the resonant wavelength that are monitored in real time. Every time a protein molecule lands on a Si microtoroid, the frequency changes.

The method is performed at room temperature, operates in aqueous environments, and measures label-free single molecules and higher concentrations on a single platform. And, the work demonstrates a range of $10^{12}$ in concentration, establishing the microcavity as a sensitive detector.

Caltech, www.caltech.edu
Recipe for Success
Carbon nanotubes are trickling into the product stream in surprising ways. The trick remains how to make more.

Imagine many of the today’s products—polymer panels, machinery and hydraulic gaskets, battery electrodes, metal tools, transistors—performing several times better without any compromise in capability. Now imagine the material needed to make this happen is so small and tricky that large-scale production is a headache. Worse, potential buyers all want specific types all featuring the same properties.

This is the exciting but frustrating reality for makers of high-quality carbon nanotubes (CNTs), the material that is attracting billions of dollars in R&D.

Nature’s strongest material, the single-wall carbon nanotube (SWNT), has a Young’s modulus nearly five times that of steel or carbon fibers and a tensile strength nearly 30 times those materials. Yet it’s less dense, flexible, corrosion resistant, non-toxic, and can be made to show superconducting characteristics. The interfacial area of CNTs is greater than that of any known material, giving a tremendous potential for strengthening materials with no cost in weight or, often, elastic properties of the original material.

Richard E. Smalley, who won a Nobel Prize for the buckeyball, a predecessor of CNTs, claimed CNTs to be “the universe’s best building material.”

Many CNT producers are out there, but few companies can deliver highly pure and applications-enabled versions of the two major types of CNTs: SWNTs and multi-wall nanotubes (MWNTs). They are manufactured in similar ways, either through arc discharge or by chemical vapor deposition (CVD), but SWNTs are far more difficult to “grow.”

“A lot of our work is focused on the fundamental problem in working with CNTs, and that’s making individual nanotubes of the right diameter, right length, and right type,” says Wade Adams, director of the Richard E. Smalley Institute for Nanoscale Science and Technology, a focal point of CNT research. “That’s the Holy Grail.”

Bound together by Van der Waals forces, CNTs like to aggregate, a bad quality for developers who want to distribute them in a composite or take advantage of the electrical properties of long nanotubes. They are also generally insoluble, and because they are black, they are resistive to both optical study and optical applications.

MWNTs are manufactured by kilograms per day and have already entered certain commercial product streams. SWNTs have tremendous potential, but remain in the hundreds of dollars per gram, and shift from CVD to floating-bed catalyst production methods will be necessary.

“There’s still a materials delivery problem. Production levels on the order of half a kilogram to 50 kg a day ensure that lower-scale and higher-cost applications will dominate” the CNT business, says Jim Tour, a chemistry professor at Rice Univ., Houston, Texas.

Nanotubes on the job
Companies are rapidly launching CNT-enabled industrial products, despite the difficulties involved.

- Carbon Nanotechnologies Inc., Houston, Texas, recently emerged from a CNT development partnership with a new CNT electrode technology for microfuel cells. The company plans to launch products within 18 months.
- NanoComposites Inc., The Woodlands, Texas, has introduced a series of CNT-infused elastomer gaskets for the oil and gas industry.
- Xidex Corp., Austin, Texas, has introduced a cantilever tip for atomic force microscopy that is made of a single 10 to 25 nm dia nanotube grown atop a silicon base. They are now developing CNT field emitting devices for scanning electron microscopes.

—Paul Livingston

Find the full length version of this article at

RESOURCES
- Rice Univ., Houston, Texas, 713-348-0000, www.rice.edu
- Xidex Corp., Austin, Texas, 512-399-9497, www.xidex.com

IMPROVING MEMBRANES

The simulated operation of a semiconductor membrane that offers more flexibility and better electrical performance than biological membranes has been reported by Jean-Pierre Leburton, Univ. of Illinois at Urbana-Champaign (UIUC). By creating nanopores in the membrane, it separates charged species or regulates the flow of charged molecules and ions, mimicking the operation of biological ion channels.

UIUC, www.uiuc.edu

BONDING WITH PROTEINS

Gold (Au) nanoparticles that are attached to multiple proteins forming sheets of protein-Au arrays have been demonstrated at Brookhaven National Laboratory (BNL), Upton, N.Y. Au nanoparticles are coated with functional organic molecules using a biocompatible linker to create specific interactions between the nanoparticles and the proteins. The nanoparticles in the protein solution are incubated to allow the nanoparticles and proteins to bind—smaller nanoparticles bind to one protein molecule whereas larger ones bind to several protein molecules.


CHANGING SHAPE WITH pH

The shape of silver (Ag) nanostructures on a quartz substrate that change by adjusting the pH value of an immersion solution has been reported at Northeast Normal Univ., China. When immersed in the buffer solution with pH 5.0, the substrate’s color changes from blue to purple, and the absorption maximum shifts from 802 nm to 503 nm. By decreasing the pH value to pH 2.2, the substrate’s color gradually changes along with its shape, going from a nanoprim to a nanodisc, turning to yellow with an absorption maximum of 432 nm.

Northeast Normal Univ., www.nenu.edu.cn