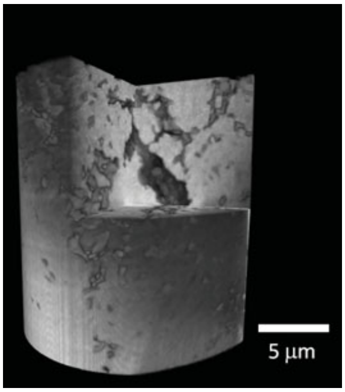


The three-dimensional reconstruction of a lithium-ion battery electrode, composed of 1441 individual images captured and aligned by the transmission x-ray microscope, reveals nanoscale structural details to help guide future energy research.

to capture every possible angle. These separate images were then combined to generate a single 3D construct of the specimen.

It is this reconstruction process that has previously limited the widespread application of transmission x-ray microscopy to nanotomography. Traditional methods require manual alignment of each 2D projection, or use software to slowly interpret the shifts. To achieve this, the sample has to have sharp internal features or be marked to provide guidelines, which can place restrictions on the materials that can be studied in this way. Such manual alignment procedures are extremely time-consuming, which limits the number of 2D images that can be employed, leading to reduced resolution of the final 3D images.

With the TXM, the specimen is mounted on top of a platform with three sensors that measure nanometer shifts in any direction as the sample rotates and the microscope takes pictures. The computer recording the images, after calibration using a gold sphere, then automatically compensates for any shifts and accurately assembles the images into the final 3D construct. The process takes only four hours, which owes more to the x-rays available from a synchrotron source than the microscope itself or the computer speed.

While this work has focused on alternative energy fuels and storage solutions, the new technology associated with this TXM will undoubtedly lead to its widespread use in examining biological, environmental, and materials samples.

Nano Focus

Multifrequency force microscopy improves sensitivity and resolution over conventional AFM

Science and technology at the nanoscale has benefited greatly from the atomic force microscope (AFM), which provides images by measuring the deflection of a probe—a very sharp tip attached to a flexible cantilever—as it scans across the surface of a sample. In conventional dynamic force microscopy (the most common form of AFM), a specific frequency is used to both vibrate the cantilever and measure the tip's deflection, but information about the sample that is encoded in the nonlinear deflection at other frequencies is irretrievable.

A solution to this problem is found in multifrequency force microscopy, where the excitation and/or deflection measurement is carried out at two or more frequencies. With acquisition times similar to those for conventional AFM, multifrequency force microscopy has the potential to overcome conventional force microscopes' limitations in spatial resolution. Recently, R. Garcia and E.T. Herruzo from the Instituto de Microelectrónica de Madrid, Madrid, Spain, have reviewed the development of five different types of multifrequency force microscopy—multiharmonic AFM imaging, bimodal AFM, band excitation, torsional harmonic AFM, and nanomechanical holography—and examined their applications in an article published in the April 1 issue of the online journal *Nature Nanotechnology* (DOI: 10.1038/NNANO.2012.38).

Multiharmonic AFM imaging is straightforward in that the higher harmonic components generated from conventional dynamic AFM are recorded and plotted. However, it is difficult to detect higher harmonics in air with the forces required for high-resolution imaging, requiring the development of special cantilevers. In liquid, where higher harmonics are easier to detect, a bacterial S-layer with 0.5 nm spatial resolution was imaged, as well as nanoscale mapping of the local stiffness and viscoelastic dissipation in living cells.

By using two excitation frequencies tuned to match two of the flexural eigenmodes of the cantilever, **bimodal AFM** separates topography from other interactions influencing the tip motion, such as magnetic or electrostatic forces, and is compatible for use in air, liquid, and ultrahigh vacuum. Operating at very low forces (50 pN) in liquid, bimodal AFM was used to obtain non-invasive imaging of isolated proteins.

The aim of **band excitation** is the acquisition of different dynamic curves while the topography of the surface is recorded. A synthesized digital signal is introduced that spans a continuous band of frequencies, while the response is monitored within the same or even larger frequency band. Although it generates a large amount of data and requires sophisticated controllers, either of which may prevent widespread application, band excitation has probed electromechanical coupling in soft biological systems by distinguishing among damping, Young's modulus, and electromechanical contributions. Ion diffusion in electrochemical batteries has also been studied with band excitation.

In **torsional harmonic AFM**, the topographic image is from conventional amplitude modulation AFM, but the tip–surface force is obtained simultaneously by integrating the higher harmonics of the torsional signal. The cantilevers are specially designed so that the tip is offset from the cantilever axis, which is beneficial for creation of torque around the axis of the cantilever and enhancing a large number of higher harmonics needed for an accurate calculation of the time-varying force. Torsional harmonic AFM has revealed fractal dimensionality of cancerous cells that differs substantially from that of normal cells.

By simultaneously exciting the sample and the probe, **nanomechanical holography** generates images of structures beneath the surface of biological or synthetic materials. The waves that propagate through the sample are scattered by internal structural features, which modify their amplitude and phase shift, and eventually emerge at the sample surface where they influence the tip–surface coupling. An image of the subsurface structure is acquired by plotting the modified phase shift as the probe moves across the sample surface. The inner structure of different cells has been imaged with nanomechanical holography as has nanoparticles inside soft materials.

According to the authors of the review article, "This new field provides a promising framework to improve compositional sensitivity and spatial and time resolution of materials in their native environment and, at the same time, allows properties that are not accessible to conventional force microscopes to be measured." They said, "Multifrequency AFM methods are conceptually more demanding than conventional AFM methods, but this would seem to be a reasonable price to pay to sustain the impressive development of force microscopy that has been seen over the past 25 years."

Steven Trohalaki

Nano Focus

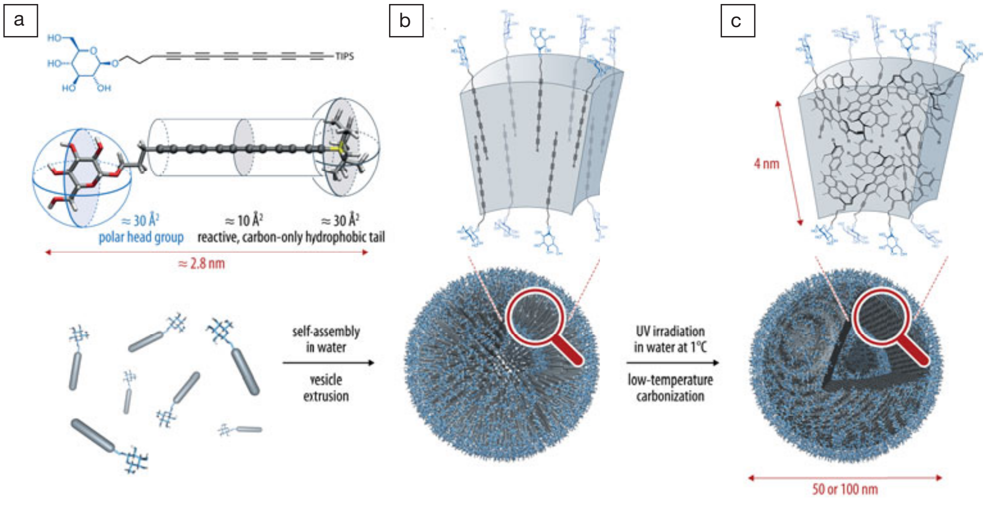
Graphite-like nanocapsules tailored

Researchers in Holger Frauenrath's group at the Ecole Polytechnique Fédérale de Lausanne (EPFL) have created carbon nanocapsules varying from 50 nm to 100 nm in diameter through a wet-chemical, UV-assisted carburization technique. R. Szilluweit, T.N. Hoheisel, and colleagues at EPFL and the Swiss Federal Institute of Technology in Zürich fabricated these capsules from amphiphilic hexaynes using a low-temperature carbonization process that allowed them to tune the size of the particles.

As reported in the March 29 online edition of *Nano Letters* (DOI: 10.1021/nl300822f), the researchers began by synthesizing the amphiphilic hexayne for use as reactive carbon precursors. In a pure state, the hexayne amphiphile was reactive and degraded at room temperature—but the researchers found that diluting the amphiphiles in dioxane/MeOH created a solution that could be kept stable at 4°C for weeks. In aqueous solution, the hexayne amphiphiles experienced a reversible and non-reactive aggregation, resulting in vesicle-like lamellar shells encapsulating a core of water. Passage of the aqueous vesicle solutions through polycarbonate membranes with 50 nm or 100 nm pore sizes and subsequent UV radiation at 1°C resulted in transformation of the self-assembled vesicles into carbon nanocapsules. Small-angle x-ray scattering, transmission electron microscopy, and dynamic light scattering experiments all confirmed they were hollow structures with 4 nm wall thicknesses and radii of 34 nm or 54 nm.

Although they were prepared at 1°C in water, the nanocapsules have an amorphous graphite carbon microstructure that can typically only be obtained by annealing at temperatures of above 600°C. The structure of the capsules may allow them to be used in high-surface area lithium-ion battery electrodes, while their biofunctional shell of carbohydrates could enable exploitation in drug delivery and cancer detection. The salient discovery, however, has to be that of the process itself, which provides "a new universal strategy for the rational preparation of tailored, functional carbon nanostructures [that] may, hence, open new possibilities for the use of carbon materials in emerging fields of technology."

Benjamin Scheiner



Wet-chemical preparation of carbon nanostructures with controlled morphology and surface chemistry. After self-assembly of the carbon-rich amphiphiles in water and vesicle extrusion, carbonization proceeds under UV irradiation below room temperature in water. Reproduced with permission from *Nano Lett.* (2012), DOI: 10.1021/nl300822f. ©2012 American Chemical Society.