

Human Hair Serves as Scaffold for TiO₂ Microtubes with Au Nanoparticles

A comparison to human hair is widely used to give a sense of scale when describing tiny structures. Now, human hair has been used as a scaffold for the fabrication of TiO₂ microtubes, as reported by S. Liu and J. He of the Chinese Academy of Sciences in the December issue of the *Journal of the American Ceramic Society* (DOI: 10.1111/j.1551-2916.2005.00615.x; p. 3513). Nanopores in the walls of the titania tubes also serve as formation sites for chemically derived gold nanoparticles.

Liu and He dipped human hairs into a solution of titanium tetrabutoxide, Ti(O_nBu)₄, in toluene or ethanol, allowing the Ti-based molecules to react with hydroxyl and amino acid groups on plate-like cells on the outside of the hair shaft. After drying and hydrolyzing the samples, the researchers repeated this sol-gel process a number of times to vary the thickness of the titania. Calcining the hair-titania samples at 800°C removed organic components, leaving behind TiO₂ tubes ~40 μm in diameter composed of platelets ~15 μm in diameter and ~0.5 μm thick, with planes perpendicular to the tube axis. X-ray diffraction analysis confirmed that the TiO₂ was crystalline, composed of roughly 2/3 rutile and 1/3 anatase phases by weight.

Close inspection with scanning electron microscopy revealed that the platelets contained nanopores ~20–200 nm in diameter. The researchers used the pores as templates for gold nanoparticles by immersing the tubes in an aqueous AuCl₃ solution and then an aqueous NaBH₄ solution. Transmission electron microscopy showed the formation of gold particles with average diameters of ~23 nm, which is consistent with the size of the nanopores.

The researchers are extending their work with the goal of improving control of the size of the metal nanoparticles and the crystalline phase of the ceramic matrix, as these properties can strongly influence the performance of the structures in proposed applications, which include catalysis, adsorption, and separation.

AMANDA GIEMANN

A pH-Sensitive Polymer Sensor Developed

In a communication in the December 13, 2005, issue of *Chemistry of Materials* (DOI: 10.1021/cm051663o; p. 6213), researchers from Seoul National University report a new polymeric sensor that detects pH changes in the physiological regime. The researchers, S.W. Hong, K.H. Kim, J. Huh, C.-H. Ahn, and W.H. Jo, describe the syn-

thesis of a poly(sulfadimethoxine) chain terminated with two fluorescent moieties, pyrene on one end and coumarin 343 on the other. Below pH 7, the polymeric spacer undergoes a rapid conformational transition to a collapsed state. This brings the fluorescent groups, which are a donor-acceptor pair, into close proximity and leads to fluorescent emission at a new wavelength, signaling the pH change. This type of sensor has numerous applications in biomedical and environmental applications, including pH monitoring of water sources and the identification of tumor cells.

Nanosensor Uses Quantum Dots to Detect DNA

Researchers at the Johns Hopkins University have developed a new method for finding specific sequences of DNA by making them light up beneath a microscope. The researchers, who say the technique will have important uses in medical research, demonstrated its potential in their laboratory by detecting a sample of DNA containing a mutation linked to ovarian cancer.

As reported in the November 2005 issue of *Nature Materials*, when a laser shines on a quantum dot, the QD can pass the energy on to a nearby molecule, which in turn emits a fluorescent glow that is visible under a microscope. But quantum dots alone cannot find and identify specific DNA strands. For that, the research team, led by J.T.-H. Wang, used two biological probes made of synthetic DNA. Each of these probes is a complement to the DNA sequence the researchers are searching for. Therefore, the probes seek out and bind to the target DNA.

Each DNA probe also has an important partner. Attached to one probe is a Cy5 molecule that glows when it receives energy. Attached to the second probe is a biotin molecule, which sticks to the streptavidin coating the surface of the quantum dot.

To create their nanosensor, the researchers mixed the two DNA probes, plus a quantum dot, in a laboratory dish containing the DNA they were trying to detect. The two DNA probes linked up to the target DNA strand, holding it in a sandwich-like embrace. Then, the biotin on one of the probes caused the DNA "sandwich" to stick to the surface of the quantum dot.

When the researchers shined a laser on the mix, some of the laser light was absorbed in the quantum dot, which passed the energy on to the Cy5 molecule attached to the second probe. The Cy5 released this energy as a fluorescent glow (see Figure 1). If the target DNA had not been present in the solution, the four components would not have joined together, and the distinctive glow would not have appeared. Each quantum dot can connect to up to about 60 DNA sequences, making the combined glow even brighter and easier to see.

"Conventional methods of finding and identifying samples of DNA are cumbersome and time-consuming," said Wang, an assistant professor in the Department of Mechanical Engineering and the Whitaker Biomedical Engineering Institute at Johns Hopkins. "This new technique is ultrasensitive, quick, and relatively simple. It can be used to look for a particular part of a DNA sequence as well as for genetic defects and mutations."

To test their technique, the researchers obtained DNA samples from patients with ovarian cancer and detected DNA sequences containing a critical mutation. "This method may help us identify people at risk of developing cancer, so that treatment can begin at a very early stage," Wang said.

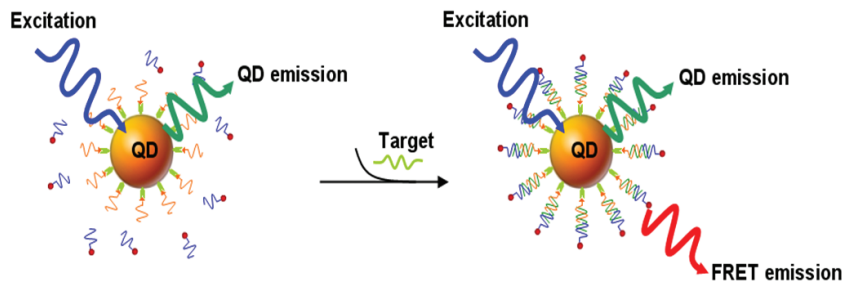


Figure 1. DNA probes capture the target strands of DNA, then stick to a quantum dot. When a laser shines on the quantum dot, the QD transfers the energy to the DNA probes, which light up through a process called fluorescence resonance energy transfer.

Hong and colleagues synthesized the polymer by atom transfer radical polymerization. They used a modified pyrene as the initiator, which fixes the fluorophore onto one end of the growing chain, and chose sulfadimethoxine as their monomer for its physiological-range dissociation constant. After polymerization, coumarin 343 was added to the free end of the chain through an ester linkage. At pH 7.5 and above, the primary emission is from the pyrene, as would be expected from the excitation wavelength of 334 nm; at pH 7.0 and below, the researchers observed a broad peak at 491 nm, corresponding to coumarin 343 emission as well. Since coumarin 343 is not excited by 334-nm light, the researchers ascribe this peak to a fluorescence resonance energy transfer from the pyrene to the coumarin due to physical proximity. This occurs as the pH is lowered below the dissociation constant of the polymer chain and the chain transitions from a coil to a globule state, pulling the two fluorophores close together. According to the researchers, this process and the appearance of the signal peak from the coumarin are reversible, suggesting that this sensor could be used to monitor multiple pH changes over time.

KRISTA L. NIECE

New Family of Self-Assembled Nanolattices Created

Inspired by the way most solids form in nature, with free-floating molecules spontaneously assembling themselves into a rigid, highly uniform array, researchers from Columbia University and IBM have learned how to create a new family of intricate structures out of artificial nanoscale crystals. Because the nanocrystals can be chosen for their precise magnetic and electronic properties, these new structures could have broad application for magnetic storage and nanoscale electronics.

"You can think of nanocrystals as building blocks like the toy Lego," said the group's spokesperson, Stephen O'Brien of Columbia, "in which a larger structure can be assembled by locking in the pieces according to their shape and the way they prefer to join to each other. Except all of this is on an incredibly small length scale—billionths of a meter."

The Columbia/IBM team has borrowed ideas from the natural world, in which the right conditions can cause the slow growth of highly uniform structures built from miniature building blocks. Opals are an example of this phenomenon: opals consist of tiny spherical building blocks of silica packed into an ordered structure.

As reported in the January 5 issue of *Nature* (DOI: 10.1038/nature04414; p. 55), O'Brien and postdoctoral research scientist Elena Shevchenko of Columbia; researchers Dmitri Talapin and Christopher Murray at the IBM Watson Research Center in Yorktown Heights, New York; and Nicholas Kotov of the University of Michigan, Ann Arbor, have formed more than 15 different binary nanoparticle superlattice (BNSL) structures using combinations of semiconducting, metallic, and

magnetic nanoparticles (see Figure 1). They demonstrated that by tuning the charge state of the nanoparticles, they were able to direct the self-assembly process.

"Combining native solutions of 6.2-nm PbSe and 3.0-nm Pd nanoparticles [with a particle concentration ratio of ~1:5] results in the formation of several BNSL structures with MgZn₂ and cuboctahedral AB₁₃ lattices dominating," the researchers reported. "However, the same nanoparticles assemble into orthorhombic AB

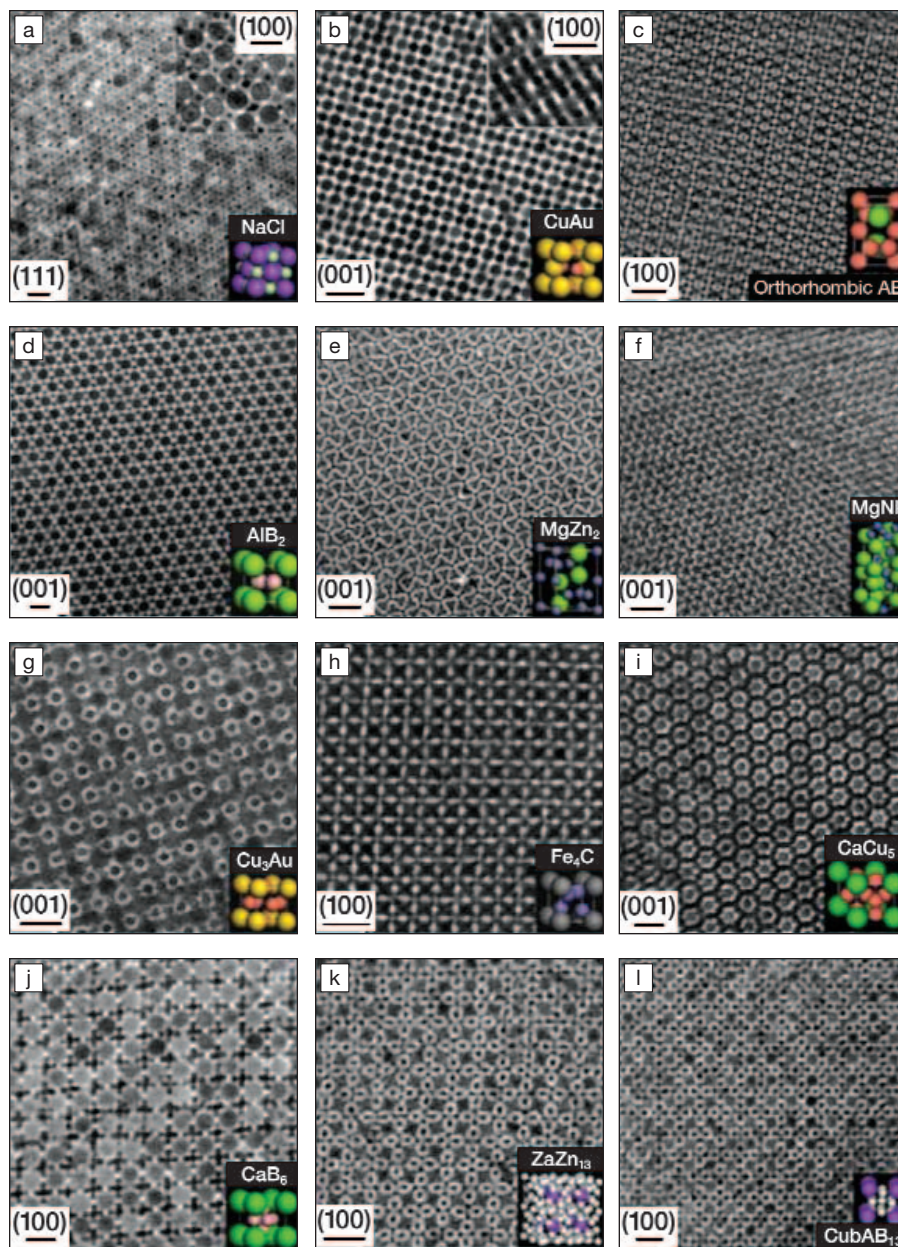


Figure 1. Transmission electron microscope images of some of the latticework structures created by the self-assembly of different nanoparticles. The colored inset image in each frame shows the corresponding three-dimensional structure in an ordinary crystal. Credit: Elena Shevchenko. Published with permission from Nature. © 2006 Nature Publishing Group.