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COLIN MCCORMICK

Researchers Examine Growth and Optical Properties of Gold Nanoparticles in Stained Glass

Stained glass is best known from its extensive use in Gothic churches, although

its production dates back to ancient civilizations of Egypt and Rome. A colored "stain" is achieved when colorless metal-doped glass is heated at high temperatures. Annealing of gold-doped glass results in the formation of colloidal gold, which gives rise to a characteristic ruby-red color through surface plasmon resonance (SPR). However, tuning the SPR

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Octahedral Nanocontainer Molecules Formed Spontaneously

Applications for nanocontainer molecules include stabilizing short-lived chemical species, accelerating chemical reactions, and directing regioselectivity and stereochemistry of reaction products. Supramolecular approaches to the self-assembly of nanocontainers, which involve hydrogen bonding or metal coordination chemistry, are efficient and quantitative. In contrast, nanocontainers constructed from cavitands (i.e., molecules whose constrained structure accommodates a cavity) typically require multiple steps. Recently, however, researchers from the Department of Chemistry and Chemical Biology at Rutgers University have used dynamic covalent chemistry to synthesize nanocontainers from 18 components in a single step and in high yield, greatly improving the simplicity and efficiency of nanocontainer synthesis.

As reported in *Angewandte Chemie International Edition* (DOI: 10.1002/anie.200504049), Rutgers University researcher R. Warmuth and co-researchers discovered a spontaneous formation of an octahedral nanocontainer (**B**), composed of six cavitands (**A**) linked together with 12 diamino bridges via 24 newly formed imine bonds (see Figure 1). Yields of up to 82% were achieved. The researchers used ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization mass spectroscopy to validate the structure of **B**. Although the researchers were unable to isolate and purify **B**, they were able to reduce all 24 imine bonds and purify the trifluoroacetate salt of the resulting polyamino nanocontainer (**C**) with reverse-phase high-pressure liquid chromatography and isolate it in an overall 63% yield. Although crystals suitable for x-ray structure determination could not be obtained, the researchers used molecular mechanics (MM) calculations to estimate the cavity volume at 1700 \AA^3 , which is large enough to encapsulate multiple guest molecules. Pulse-field gradient spin-echo NMR measurements and application of the Stokes–Einstein equation yielded a solvodynamic diameter of 3.2 nm, which is consistent with the MM model. The researchers also used MM to show that the formation of **B** requires each ethylenediamine to be in an *anti* conformation.

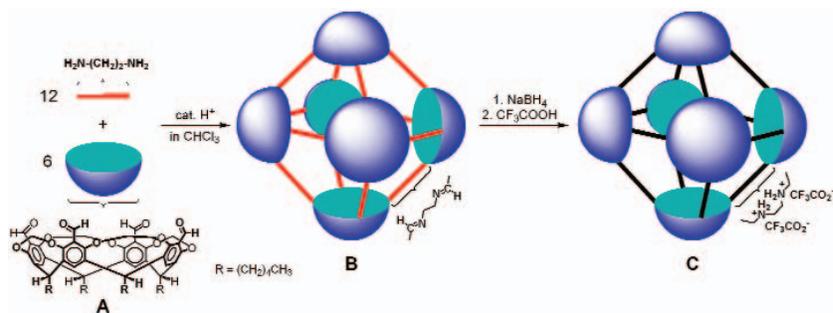


Figure 1. An octahedral nanocontainer (**B**) composed of six cavitands (**A**) linked together with 12 diamino bridges via 24 newly formed imine bonds; **B** is reduced to polyamino nanocontainer (**C**).

The researchers said, "We see potential uses for [**C**] and analogues in drug- or pesticide-delivery systems, wastewater detoxification, separation technology, and as molecular reactors for controlled oligomerizations of organic and inorganic molecules." In addition, the researchers said that "other covalent nanoassemblies with spherical or tubular shapes and different properties could be accessible through such multicomponent synthesis."

STEVEN TROHALAKI

peak in stained glass requires very long annealing times that also result in a deteriorated shape of the gold clusters. In the December 9, 2005, issue of *Angewandte Chemie International Edition* (p. 7905; DOI: 10.1002/anie.200502174), M. Eichelbaum at Humboldt-Universität zu Berlin, R. Müller of the German Federal Institute for Materials Research and Testing, and their colleagues have shown that activating the gold-doped glass with hard x-ray radiation reduces the annealing time needed for tuning the SPR peak, thereby minimizing shape degradation of the gold clusters.

Gold-doped glass was obtained by melting 0.02 mol% AuCl₃ with soda-lime silicate glass. Annealing at 590°C for 1 h produced ruby-colored glass with the SPR peak at 574 nm. Another 4 h of annealing was required to observe a shift

of 6 nm (to 580 nm) in the SPR peak, and high-resolution transmission electron microscopy images confirmed that this caused distinct deviation of particle shape from spherical symmetry. In contrast, when the gold-doped glass was activated by x-ray radiation (32 keV) for 5 min, only 30 min of annealing produced a red-colored glass with a SPR peak at 540 nm. Also, substantial changes in SPR peak positions were observed for short annealing periods: the SPR peak shifted to 547 nm after 10 min of annealing at 590°C, and to 554 nm after 15 min of annealing at 630°C. Although the shifts in SPR peaks were explained by the deviation of the gold clusters from their spherical shape, samples activated by x-rays still exhibited a sharp size distribution of gold clusters because of the shorter annealing period. Short annealing periods are due to the presence of a

very high density of gold atoms that are produced when cationic gold is reduced by x-ray radiation. X-ray near-edge spectroscopy confirmed that the x-ray-activated samples have very small quantities of Au³⁺ ions and mostly solid gold. The researchers said that x-ray-activated stained glasses are sturdy components for realizing optically tunable devices in integrated nanophotonic applications.

TUSHAR PRASAD

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News of MRS Members/Materials Researchers

Willard S. Boyle and **George E. Smith**, both formerly of Bell Laboratories, share the **Charles Stark Draper Prize**—a \$500,000 annual award that honors engineers whose accomplishments have significantly benefited society—“for the invention of the charge-coupled device (CCD), a light-sensitive component at the heart of digital cameras and other widely used imaging technologies.”

Douglas B. Chrisey, formerly of the U.S. Naval Research Laboratory, has been named the Deputy Director for Research and Development at the Center for Nanoscale Science & Engineering at North Dakota State University.

Joseph A. Gardella Jr., State University of New York at Buffalo, received the 2005 *Presidential Award for Excellence in Science, Mathematics, and Engineering Mentoring*.

This presidential award recognizes individuals who have demonstrated a commitment to mentoring students and increasing the participation of minorities, women, and disabled students in science, mathematics, and engineering.

Ashok Puri, University of New Orleans, received the 2005 *Presidential Award for Excellence in Science, Mathematics, and Engineering Mentoring*. This presidential award recognizes individuals who have demonstrated a commitment to mentoring students and increasing the participation of minorities, women, and disabled students in science, mathematics and engineering.

David H. Sliney, program manager for the U.S. Army Center for Health Promotion and Preventive Medicine Laser/Optical Radiation Program, received the

24th Arthur L. Schawlow Award from the Laser Institute of America (LIA) during ICALEO 2005 (the International Congress on Applications of Lasers & Electro-Optics), which was held last October. The award is in recognition and appreciation of Sliney's extensive contributions as a pioneering leader in the field of laser safety for more than 30 years and as one of LIA's most valuable supporters.

Daniel Zajfman has been nominated as the next president of the Weizmann Institute of Science in Rehovot, Israel. In accordance with the rules of the Institute, the election of the president will be approved by the full board. Zajfman will serve as the 10th president of the Weizmann Institute, replacing the Institute's current president, Ilan Chet, whose term of office ends in December 2006.

Scientific American named its top contributors to science and technology in 2005, including:

Edward H. Sargent (University of Toronto), **Michael Grätzel** (Swiss Federal Institute of Technology), and **Tsutomu Miyasaka** and **Takuro N. Murakami** (Toin University of Yokohama) for their research in energy and to Hydrogen Solar for its business in energy;

Inez Y. Fung (University of California, Berkeley) for research in protection from the Earth's climate;

Paul W.M. Blom and **Ronald C.G. Naber** (University of Groningen and

Philips Research Eindhoven), **John Rogers** (University of Illinois at Urbana-Champaign), and **Samuel I. Stupp** (Northwestern University) for research on plastic; and

Bradley J. Nelson (Swiss Federal Institute of Technology) and the **U.K. Royal Society and the Royal Academy of Engineering** for research in nanotubes, and **James E. Jaskie** (Motorola Physical Sciences Research Laboratory, **DuPont Central Research and Development**, and **Hewlett-Packard Laboratories** for their business contributions in the area of nanotubes.

Corrections

In the December 2005 issue of *MRS Bulletin* 30 (12) p. 965, the reference immediately following 105 was incorrectly numbered as 109; it should be 106. In the same issue, pp. 964–966, in References 17, 23–25, 30, 44, 52, 71, 73, 82, 104, 106 (corrected number), 108, 109, 111, and 112, the name T.P. Russell should have appeared instead of P.F. Green.

The Center for Nanoscale Materials at Argonne National Laboratory will begin initial operations in April 2006 and full operations in September 2007. Incorrect dates were published in the UP CLOSE article in the January 2006 issue of *MRS Bulletin* 31 (1) p. 44.