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ACHEMA Takes A Look At Nanomaterials

Symposium, exhibition spotlight developments in nanoparticle production technology

Michael Freemantle

Nanomaterials is a big business−and growing, proclaimed Degussa's Harald Häger at ACHEMA 2006, the international trade fair for the chemical process industries that was held in May in Frankfurt, Germany (C&EN, July 3, page 31).

Photo By Michael Freemantle

GRINDING
NETZSCH-Feinmahltechnik displays its agitator bead mill,ZETA RS, for nanoparticle production, at ACHEMA 2006.

Several business studies put the market value for nanomaterials in 2002 at around $23 billion, observed Häger, who is vice president for process and product development at Degussa's High Performance Polymers business unit. At an ACHEMA symposium on the processing and production of nanomaterials, he said studies predict that the total market value for nanomaterials in 2006 will be more than $30 billion, with nanocomposites accounting for $380 million to $1.2 billion.

As the nanomaterials business continues to expand, new processes are being developed for their production. At the same time, there are increasing concerns about health, safety, and environmental issues relating to nanoparticles.

Not all nanomaterials are new. Biomaterials with nanometer-scale dimensions have existed on Earth as long as life has. Some manufactured nanomaterials have also been around for some time. For example, the first commercial nano-reinforced tires were introduced during World War I; the nanomaterial was carbon black. Today, many consumer products, including creams, sprays, and cosmetics, contain nanoparticles.

Technology is now being exploited to produce nanomaterials having improved electrical conductivity, catalytic activity, hardness, scratch resistance, and self-cleaning capabilities, according to an ACHEMA 2006 trend report. Nanotechnology applications are also being developed to enhance the performance of gas sensors and other industrial monitoring devices and to produce better fuel cells and lighter weight and longer lasting batteries, the report notes.

In the medical arena, an imaginative array of nanoscale particles are being investigated to deploy potent cancer-killing drugs more effectively in the human body. Nanoparticles, the report notes, accumulate preferentially within tumors and other cancerous cells, spare healthy surrounding tissue, and minimize the devastating side effects often associated with chemotherapy and radiation-based cancer treatments.

Not surprisingly, in view of these diverse applications, many universities, industrial companies, and government bodies are stepping up their activities and investing heavily in nanotechnology R&D.

In April, for example, BASF opened its first research center for nanotechnology in Asia: the Competence Center for Nanostructured Surfaces in Singapore. The new center will employ 20 staff, mainly scientists and technicians, and concentrate on nanostructured surface modification for a variety of applications, including a possible solution to the problem of biofouling on ship hulls and other marine surfaces.

BASF plans to spend around $230 million in nanotechnology research worldwide between 2006 and 2008, according to the company's research executive director, Stefan Marcinowski.

At the ACHEMA symposium, BASF senior scientist Jens Rieger outlined the company's current activities in nanomaterials. BASF, he said, is investigating processes for generating nanostructures that can be incorporated into coatings, emulsions, dispersions, plastics, and other products. Nanomaterials provide these products with improved properties, such as better mechanical strength and higher heat resistance, or novel ones, such as dirt repellency and water vapor permeability.

Rieger Schild

The synthesis of cube-shaped nanostructures that can store comparatively large amounts of hydrogen is also attracting the attention of BASF researchers. The nanocubes are three-dimensionally linked organometallic networks that are highly porous. "Nanocubes could be used as a rechargeable storage medium for miniaturized fuel cells," Rieger noted. "They might also replace the rechargeable batteries that are currently used in laptop computers, cell phones, and other mobile electronic devices."

He added that BASF is also interested in developing nanocomposite dispersions that can be used for scratch-resistant coatings and nanofoams for heat insulation.

Six methods are widely used for producing nanoscale particles, according to the ACHEMA trend report. They are mechanical crushing, plasma arc and flame pyrolysis methods, chemical vapor deposition, electrodeposition, sol-gel synthesis, and the modification of naturally occurring nanomaterials such as zeolites.

At the ACHEMA exhibition, several companies displayed equipment for producing nanomaterials. For example, Willy A. Bachofen, a company headquartered in Basel, Switzerland, which specializes in dispersion and grinding technology, exhibited a new mill called Dyno-Mill NPM. The machine uses ultrafine grinding beads to break up 20- to 50-µm particles in dispersions to particles smaller than 100 nm. Applications listed in the company brochure include the preparation of nanomaterials used in paints, printing inks, dental fillings, and the dissolution of active ingredients for cancer therapy.

The German firm NETZSCH-Feinmahltechnik also displayed a new mill for grinding to the nanometer scale. The agitator bead mill, ZETA RS, employs wet grinding technology to produce particle sizes in the range of 40-100 nm. Solid particles in a suspension are ground into nanoparticles by impact and shearing forces between moving grinding beads. The agitator shaft transmits kinetic energy to the beads, which are available in materials such as plastics, glass, ceramics, steel, and tungsten carbide. The appropriate material is selected to avoid contamination of the nanoproducts.

At the symposium, Stephan Barcikowski, a group head at Laser Zentrum Hannover, in Germany, described the use of ultrafast lasers for the continuous production of nanomaterials. Direct laser-based production of nanoparticles in liquids is highly attractive compared with conventional nanoparticle production technologies, because no chemical precursors are required, he said. The method is particularly promising for the production of pure nanoparticles for biomedical, cosmetic, and automotive applications, he added.

The method typically relies on the use of a femtosecond or picosecond pulse laser in streaming liquid or gaseous media. Barcikowski's group has applied the technique to produce nanoparticles of metals like titanium and silver, as well as alloys and ceramics, in solvents such as water, acetone, and dichloromethane. The group has also used the technique to generate aerosols containing nanoparticles of alloys or polymers such as polystyrene.

"In the case of ultrashort pulse laser ablation, the solid is the bulk material," in the form of chips or foils, Barcikowski noted. "The matrix can be any infrared-transparent liquid in which in situ dispersion and stabilization of the primary particles takes place."

In another lecture at the symposium, Marko Buchholz, head of development and application technology at Ekato Unimix, Schopfheim, Germany, outlined the use of a high-pressure homogenizer, known as the Ekato Nanomix, for generating stable emulsions containing nanoscale droplets for use in the cosmetic, food, beverage, and pharmaceutical industries. The process involves the use of a premix container and homogenizer to prepare a homogeneous mixture of the continuous and disperse phases and a surfactant. Two jets of the liquid are then injected at high pressure in opposite directions through two nozzles into a stabilization chamber. The two jets collide, and the resulting turbulence deforms and breaks up the dispersed droplets. The resulting nanodroplets are stabilized by the surfactant and therefore do not coalesce.

The patented Nanomix technology, which is scalable from 500 mL per hour to more than 10 m^3 per hour, can also be used to prepare stable suspensions of nanoscale solid particles and to break open cells in biotechnological processes.

Andreas Voigt, a researcher at Otto von Guericke University of Magdeburg, Germany, has been investigating the use of microemulsions for producing nanoparticles, in collaboration with researchers at Max Planck Institute of Dynamics of Complex Technical Systems in Magdeburg. He uses microemulsions consisting of water, cyclohexane, and a nonionic surfactant. The droplets can act as nanoreactors. They are especially suited for production of nanomaterials by precipitation because they provide a closed environment that is retained in a liquid, Voigt said.

Last year, he and his colleagues reported on the precipitation of barium sulfate nanoparticles from the aqueous solutions of barium chloride and potassium sulfate reacting in microemulsions (*Chem. Eng. Sci.* **2005,** *60*, 3373). $BaSO_4$ is a relatively simple inorganic material that has been used extensively to investigate precipitation phenomena. It is suitable for many applications, including fillers in paints and plastics and in pharmaceutical formulations, the authors noted.

Photo By Michael Freemantle

NOTHING COULD BE FINER
Willy A. Bachofen AG has developed a new mill, Dyno-Mill NPM, which employs ultrafine grinding beads.

The aim of the study was to elucidate the influence of process control parameters on product properties such as particle size, size distribution, and particle shape. The parameters include temperature; feeding and stirring rates; feeding sequence; molar ratio of initial reactant concentrations; and water, cyclohexane, and surfactant fractions in the microemulsion. The team concluded that the molar ratio of initial concentrations of $BaCl_2$ and K_2SO_4 is one of the most important factors in determining $BaSO_4$ particle size.

The driving force behind these research activities is to scale up this approach from laboratory to production with corresponding control of the process and product, Voigt told C&EN.

At the Technical University Berlin, chemist Sebastian Polarz and coworkers at Ruhr-University Bochum, in Germany, have been exploring how chemistry is influenced by confinement in small spaces such as nanosized compartments in mesoporous materials.

Inorganic porous materials such as silica, organically modified silica, or transition-metal oxides typically are characterized by a narrow pore size distribution on the order of 2-50 nm, high porosities, and large pore volumes and surface areas, Polarz noted in a lecture.

"Only a small number of particles can be present in each pore," Polarz told C&EN. These materials open up interesting possibilities for the preparation of nanocrystalline particles that are effective in heterogeneous catalysis, he added.

Last year, the German team reported the preparation of size-selected zinc oxide nanocrystals inside the "wormhole" pore systems of ordered mesoporous silica materials (*J. Am. Chem. Soc.* **2005,** *127*, 12028). The ZnO/SiO_2 nanocomposite materials are synthesized from a liquid precursor prepared by reacting dimethylzinc with methoxyethanol in dry toluene. The spatial confinement of the mesopores restricts the growth of the ZnO particles to the size of the pores and enhances the dispersity of the particles.

The team has also been looking into the use of mesoporous materials as model systems to prepare Cu/ZnO nanocomposite catalysts for the synthesis of methanol from carbon monoxide and hydrogen. When Cu and ZnO are confined in small spaces, the density of the active catalytic species at the interface of the Cu and ZnO particles increases, Polarz said. As a result, the catalytic activity of the nanocomposite particles is greater than that of Cu/ZnO composite catalysts used in industry for methanol synthesis, he said.

Influencing the size of nanoparticles is also of interest to Marco Zanella, a Ph.D. student who has been working with Wolfgang J. Parak's group at Ludwig Maximilians University, Munich, Germany, in a collaborative project with a group led by Liberato Manna at the National

Nanotechnology Laboratory in Lecce, Italy. The team has been developing methods for synthesizing fluorescent colloidal semiconductor nanoparticles, which are used in applications such as biolabeling and photovoltaics. So far, achievable fluorescent colors have been limited mainly to the spectral range from green to infrared, Parak told C&EN.

At ACHEMA, Zanella outlined a simple route for preparing high-quality blue fluorescent nanocrystals of specific sizes that have a cadmium selenide core and zinc sulfide shell. "Depending on the nanocrystal's size, the emission color extends from the blue to the red region of the spectrum, and the quantum yield and stability of the nanocrystals are increased if a shell of higher band-gap material such as ZnS is grown around the CdSe cores," he noted.

The CdSe nanocrystals are prepared from cadmium oxide and selenium and are grown at 80 ^{o}C in a solution containing surfactants. The ZnS shells are then grown on size-selected nanocrystals. "The growth of small clusters of CdSe is not continuous but quantized," Parak explained. "We refer to these stable configurations of particles as 'magic size clusters.' "

In a paper yet to be published, the German and Italian researchers report the fabrication of a blue-light-emitting diode in which the active layer is a blend of the blue-emitting CdSe/ZnS nanocrystals and a diphenylcarbazole.

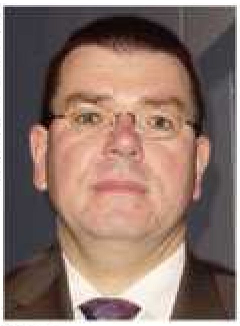
In a symposium session on nanocomposites, Christoph Schild, director of materials technology at Bayer, outlined the company's activities in nanostructured materials. He described, for example, Dispercoll S dispersions, which were introduced by Bayer a few years ago. The dispersions, which contain SiO_2 particles between 9 and 55 nm wide, are used in the formulation of aqueous adhesives over a broad viscosity range for use in the furniture, automotive, shoe, and construction industries.

Bayer is also scaling up a process for producing high-purity multiwalled carbon nanotubes, branded Baytubes. The process involves blowing a carbon-containing gas, such as methane or ethane, into a reactor oven filled with a catalyst. The reactor capacity is currently being scaled up, according to Schild. The increased capacities will enable the carbon nanotubes to be produced in bulk at relatively low cost, he said.

The company is also active in nanobiotechnology. It has developed aqueous fluorescent dye dispersions of crystalline nanoparticles with embedded lanthanide ions, such as terbium or europium ions. When stimulated by light, the ions emit light of a specific wavelength depending on the ions used. "These nanophosphors are highly stable and can be used as fluorescent markers that dock onto DNA strands or antibodies," Schild said. The goal is to use these markers to diagnose cancer or infectious diseases.

Bayer is stepping up its activities in nanotechnology, according to Harald Pielartzik, head of Bayer's competence center that coordinates company-wide nanotechnology activities. "Our goal is to become a developer and supplier of nanotechnology to the global markets for precision materials, health care, and nutrition," he noted in a news release earlier this year.

PHOTOS BY MICHAEL FREEMANTLE



Häger

Krug

The German firm is one of 13 partners participating in a research project known as NanoCare, which aims to investigate the safety of nanomaterials and the effects of industrially produced nanoparticles on human health and the environment (C&EN, May 1, page 10). The German Federal Ministry of Education & Research and German industry are contributing more than $6 million and $3 million, respectively, to the three-year project, which was launched in March.

The project coordinator is Harald F. Krug, professor of molecular toxicology at Germany's Karlsruhe Research Center. He carries out research on the biological behavior of nanoparticles, their mechanisms of uptake, and their distribution in cellular systems.

"We are all exposed to nanomaterials," he said at ACHEMA. "Man-made nanostructures are being specifically engineered to interact with biological systems for particular medical or biological applications." Since the 1970s, there have been many studies on the use of nanomaterials for treating diseases, he observed. Not all the materials are degradable, and some stay in the body for long periods. A good local and systemic tolerance during and after medication should be a condition of their use, he urged.

The large-scale generation of nanoparticles may affect a wide range of organisms throughout the environment, Krug noted. The increasing production, particularly of metal oxide nanoparticles and new carbon materials, will lead to greater exposure at workplaces, at packing stations, and during applications of the products, he said. "In addition, waste treatment and containment at the end of a product's life cycle must also be considered. For these reasons, it is important to determine how nanomaterials that come into contact with living organisms are taken up, transported in and through cell layers, and affect biological functions.

"There is a huge need for more research on the impact of nanomaterials on the environment and biological systems," Krug concluded.

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