Bacterial Templates and Sonochemistry Used to Form Hollow ZnS Nanostructures

The unique physicochemical properties displayed by hollow nanostructures make them interesting candidates for optical, sensing, electronic, and drug-delivery applications. Templates typically employed in hollow-nanostructure fabrication are comprised of synthetic materials or natural organisms, but each route has drawbacks. The complicated routes required for synthetic templates make intricate morphologies, which may display remarkable properties, currently unattainable. In addition, template removal requires multiple steps, consumes energy, and sometimes results in nanostructure collapse. Recently, however, H. Zhou, T. Fan, and D. Zhang at Shanghai Jiaotong University, China and Q. Guo and H. Ogawa at Saga University, Japan, have developed a sonochemical method for the fabrication of hollow ZnS nanospheres and nanotubes in one step at room temperature, inclusive of core removal, using bacteria as templates. The researchers said that extension of the method to other bacteria that display much more complex morphologies should be straightforward.

As reported in the May 1 issue of *Chemistry of Materials* (p. 2144; DOI: 10.1021/cm0629311), the researchers used as sacrificial templates *Streptococcus thermophilus*, which is spherical with a diameter of 0.5–0.9 μm, and *Lactobacillus bulgaricus*, which is tubular with dimensions of ~1–5 μm in length and ~0.3–0.8 μm in width. The bacteria were suspended in an aqueous solution containing thioacetimide and zinc acetate and sonicated for 6 h. Core–shell structures are formed in the first stage of the process, where ZnS nanoparticles deposit onto the cell surfaces due to interactions between the surface functional groups and the chemical precursors produced under sonochemical conditions. Cell disruption occurs in the second stage and, in the last stage, cellular fragments escape into the solution through pores in the ZnS shells, leaving hollow nanostructures.

The researchers also observed results of two other types of outcomes. Twin hollow nanostructures form when the fabrication process occurs when a cell is dividing in two. In addition, gaps in the ZnS shell, which the researchers said are due to either incomplete shell formation or shell breakage, result in broken, hollow nanostructures.

The researchers used field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) to show that the nanostructures formed using *Streptococcus thermophilus* as templates are approximately spherical with diameters ranging between 0.5–0.9 μm. Micrographs showing the apparent cavities of broken nanospheres demonstrate their hollow nature. TEM images of both hollow nanospheres and nanotubes show that shells with thicknesses of ~70–80 nm are formed when the cell surfaces are coated with ZnS nanoclusters ~60–70 nm in diameter. Diffuse rings in the electron diffraction pattern of hollow ZnS nanospheres demonstrate a polycrystalline structure. The researchers tried substituting zinc acetate with zinc chloride or zinc nitrate but were unsuccessful, which led them to hypothesize that the acetate ligand plays an important role in grafting zinc onto cell surfaces. The researchers proposed a scheme of sonochemical reactions that is consistent with their results.

The researchers expect that their method can be extended to "templating other shapes of bacterium such as vibrios, spirillum, square bacteria, fusiform bacilli, and a similar approach is applicable to other materials like metal chalcogenides, amorphous or crystalline metal oxides, metals or alloys based on the similar mechanism," and would "open up the possibilities for extensive study of the physical and chemical properties of these hollow nanostructures and their potential applications."

STEVEN TROHALAKI

Wetting Intergranular Films Formed by Impurities Accelerate Single-Crystal Conversion in Alumina

S.J. Dillon and M.P. Harmer from Lehigh University have reported in the March issue of the *Journal of the American Ceramic Society* (p. 993; DOI: 10.1111/j.1551-2916.2007.01510.x) the conversion of polycrystalline Al_2O_3 capillary tubes doped with 500 ppm MgO into single crystalline Al_2O_3 through controlled abnormal grain growth at temperatures between 1670°C and 1945°C in N_2-H_2 atmospheres for 0–2 h.

The capillary tubes had a 1.25 mm inner diameter, a 3.30 mm outer diameter, and a length of 30 mm, and were mounted vertically on the end of a 0.1 mm diameter molybdenum wire for the solid state conversion while heating and cooling them at a rate of 16.5°C/min. Samples to be observed by transmission electron microscopy were quenched at the end of their anneal to preserve their high-temperature structure. The resulting single crystals were up to 30 mm in size, only limited by the hot zone of the furnace, with their basal plane oriented ~90° or ~45° with respect to the tube axis, and with curved boundaries on all scales and rough on the atomic scale. The researchers measured grain boundary velocities of up to 1.67×10^{-5} m/s, which constitute the most highly mobile alumina grain boundaries measured to date.

"At such high velocities, pores, second phase, and entire grains separated from the growing single crystal interface and were entrapped in the grains. This suggests that slow processes such as pore drag, drag from liquid in triple pockets, and immobile grains did not significantly affect the mobility," the researchers said. CaO impurities segregated to the boundary between the single crystal and the polycrystalline region, forming a wetting intergranular amorphous film, 10–20 nm thick, that facilitated single-crystal conversion and demonstrated that the mobility of the grain boundary is controlled by diffusion through this film. Such a film was not observed around normal grains in front of the growing single crystal in samples sintered for 0 h. This situation is analogous to diffusion-controlled liquid-phase sintering with a short path length, and measured grain boundary mobilities correspond reasonably well with those calculated for this situation, said the researchers. However, the researchers said that discrepancies arise between the activation energies of the calculated and measured mobilities, which the researchers speculate may result from constraints imposed by the confinement of the liquid to a ~10 nm intergranular film.

Corrections

In the article "The Mechanics and Physics of Defect Nucleation" by J. Li in the February 2007 issue (*MRS Bulletin* **32** (2), 151–159 (2007)), on p. 155, σ(σ) should be Ω(σ). Also on p. 155, "mobile" is replaced by "glissile" in the following:

These preexisting defects must be sessile—for example, Lomer–Cottrell locks, other sessile dislocation structures,[72] vacancies—because if they were glissile they would move away from the high-stress region very quickly, before heterogeneous nucleation can occur. It would still require very high stress, a significant fraction of the ideal strength, to nucleate glissile dislocations out of these originally sessile structures.[72,84]

On p. 158 in Li's article, the partial derivative symbol ∂ was omitted from the expressions $-Q/\sigma^*$, $-Q/\sigma$, and σ/σ^*. The correct expressions are $-\partial Q/\partial\sigma^*$, $-\partial Q/\partial\sigma$, and $\partial\sigma/\partial\sigma^*$. On p. 158, Reference 37 is published as T. Zhu, J. Li, A. Samanta, H.G. Kim, S. Suresh, *Proc. Natl. Acad. Sci. USA* **104** (2007) p. 3031.