Nano Ceramics Center, National Institute for Materials Science

The Nano Ceramics Center was launched as a research center of the Nanoscale Materials Field at the National Institute for Materials Science (NIMS). In recent years, there has been strong demand for the development of novel devices and equipment that support advanced industries such as IT/semiconductors, the environment, nuclear power, aerospace, and others, along with the achievement of higher efficiency and the reduction of environmental damage. We intend to fabricate innovative ceramics with novel individual properties and/or multifunctional properties including electric, dielectric, thermal, optical, chemical, and mechanical properties through the development of nanoparticle processing. The Center consists of the following six groups. Fine Particle Processing Group, Non-Oxide Ceramics Group, Nitride Particle Group, Fine-Grained Refractory Materials Group, Plasma Processing Group, and Functional Glass Group.

In the 2nd Mid-Term Program target period (FY2006–2010), the Nano Ceramics Center is responsible for the “fabrication of innovative ceramics through advanced nanoparticle processing” project. Here, our aims are to develop several methods of nanoparticle processing originally developed at NIMS and to develop techniques of evaluating and designing grain-boundary nanostructures. Furthermore, by the organic collaborative work among each subproject, we intend to create innovative ceramics. The fundamental technologies that are key to achieving these aims are (1) the synthesis of nanoparticles with uniform composition and controlled crystallite size, (2) the arrangement/assembly and dispersion control of nanoparticles with controlled particle size, (3) the precise structural control at all levels from the micrometer to the nanometer order, and (4) the nanostructural design based on theoretical/experimental studies of the correlation between the local structure and functions of interest. The relationships among these elements are shown in Fig. 1. In particular, it is now understood that the application of external stimulation, such as magnetic energy, electric energy, and/or stress to a reaction field is effective in realizing advanced nanoparticle processing.

NIMS has a history of pioneering research and boasts high potential in its areas of study. Concrete element technologies include nanoparticle synthesis using thermal plasma, precursor preparation, functional nonoxide nanoparticle synthesis using gas-phase reactions, advanced sintering techniques, nanostructure design by simulation, the fabrication of nanoparticles and/or amorphous particles by high-energy ball milling, the orientation of weakly magnetic ceramics under a strong magnetic field, layer formation by electrophoretic deposition, nanoparticle assembly, the fabrication of nanopore arrays by anodic oxidation, and grain boundary evaluation techniques. Here, we would like to introduce some of the research achievements at the Nano Ceramics Center that are not covered in this special issue.

Particle preparation

Nonoxide ceramics including SiC, Si₃N₄, and SiAlON have been known as engineering ceramics but nowadays they have applications for the IC industry, environmental materials, and next-generation phosphors. Regarding the application of SiAlON phosphors, three manuscripts are presented in this issue. For the application of SiC-based ceramics to IT/semiconductor industries, high-purity fine powders and a large-scale, complete densification sintering technique are required. In powder synthesis, we use organic liquids as raw materials in place of conventional minerals.
We have synthesized resin precursors by the sol–gel process and succeeded in converting these to SiC and other ceramic powders at high temperatures [1]. This process makes it possible to produce powders having extremely high purity that are sufficiently fine for sintering at low cost (Fig. 2). We are engaged in the development of unique plasma-generating methods, the plasma synthesis of nanosized particles, and the development of techniques for assembling functional structures from nanoparticles. Details are described in this special issue.

Arrangement/assembly

Our objectives are to establish the basic technologies for fabricating controlled structures from the nano- to the micrometer order by bottom-up methods using nanoparticles in solution and nanospace, and to fabricate precisely controlled structures with outstanding properties at various levels from the 0-dimensional to the 3-dimensional. To achieve these objectives, we are conducting research including (i) the fabrication and assembly of nanoparticles, (ii) the microspace control and creation of laser oscillation devices using nanoparticles and organic/macromolecules, (iii) the arrangement, assembly, and pseudo-single crystal techniques for weakly magnetic ceramics by the advanced...
Fig. 4. Schematic illustration of circularly polarized laser emission from the dye-doped chiral liquid crystal by irradiation with a linearly polarized light.

Fig. 5. Alumina cap in which the outer shape of the substrate is transcribed, and a free-standing film, on which the surface pattern of a coin was transcribed.

Fig. 6. Schematic of intelligent anodic oxidation technique.
use of strong magnetic fields, and (iv) the fabrication of highly controlled structures by external field-controlled colloidal processes.

The field of surface chemistry using organic-monomolecular systems has witnessed tremendous growth not only in the understanding of the fundamental chemistry but also in the potential of technological applications [2]. Fig. 3 shows an organic monomolecular film covalently attached to bare silicon. The organic nanofilm, which is sandwiched between a platinum film and silicon, forms an atomically flat interface with the outermost silicon layer. Such organically functionalized semiconductors provide a large number of valuable opportunities to (1) chemically passivate a light-emitting semiconductor surface, (2) detect specific molecular or biochemical interactions generated between a terminal group serving as a host and a guest molecule by changing an electric signal, and (3) emit electric or photon energy through organic wires. We aim to extend the contribution that surface chemistry makes to the development of nanoscience.

We have developed self-organized photonic crystal (PhC) structures of organic and polymeric materials for laser applications. Chiral liquid crystal molecules and monodispersed polymer microparticles can spontaneously assemble 1-D and 3-D PhC structures, respectively. The photoexcitation of a chiral liquid crystal cell with linearly polarized light gives rise to circularly polarized laser emission at the photonic band edge(s), as shown in Fig. 4 [3]. The optically excited laser action can be controlled by external stimuli such as the application of a voltage and irradiation with UV light. Moreover, we have found novel uses of 3-D PhC structures comprising polymer microparticles, such as for the fabrication of laser devices. The introduction of an intermediate light-emitting layer between the 3-D PhC films leads to efficient laser action on the basis of defect mode in the photonic band-gap effect [4]. This procedure enables the fabrication of all-plastic laser devices. A current objective is to generate highly efficient laser emission by combining self-organized polymer PhCs with light-emitting materials such as organic dyes or inorganic fine particles.

When an electrical field is applied to charged particles in a solvent, the particles migrate by electrophoresis to the electrode of the opposite polarity and then coagulate on the surface of the electrode. This technique is known as electrophoretic deposition (EPD) and is suitable for fabricating film and laminated layers using nanoparticles. By applying electrical conductivity by coating or patterning conductive polymer films on preshaped insulating ceramics, we succeeded in directly shaping colloidal ceramic particles on substrates by EPD [5]. Examples of fabricated ceramics are shown in Fig. 5.

Ordered pore modification

Anodic oxidation is a technique that is used to apply color and improve the durability of aluminum products, and has long been referred to as the aluminite technique. In the present project, our objective is to develop an “intelligent anodic oxidation technique”, which expands the conventional aluminite technique to nanotechnology [6]. Fig. 6 shows this technique schematically. Hole-size uniformity, a precise hole cross-sectional shape, and the improvement of reproduction accuracy in repeated treatment are achieved by computer control of the voltage, temperature, type of acid, blending ratio, and strength of acid used in reactions, and multiple combinations of these items.

Two methods are mainly used to introduce chemical compounds into microholes. In one method, which is used with comparatively large holes (>50 nm), solubility and surface tension are the important elements. This method is used to introduce substances in liquid form into holes. A high-performance photocatalyst in which TiO2 was introduced was prepared using this method. The second method is an electroplating technique. This is a method of accumulating an electrically charged compound

![Fig. 7. Nanorods and nanotubes prepared using a film fabricated by anodic oxidation as a mold.](image-url)
at the bottom of the holes by setting electrodes there. This technique is suitable for producing magnets with ultrafine, comparatively long shapes (diameter: several nm, length: several μm). The ability to produce microscopic structures with this type of large aspect ratio is a strength of this technique. Fig. 7 shows photographs of TiO2 nanotube and Ni nanorod assemblies prepared by this technique.

**Microstructure control**

Recently, high magnetic fields with a field strength of up to 14 T have been readily available without the use of liquid helium due to the development of superconducting technology. These new magnets have been used in studies in many fields, including crystal alignment, levitation, and separation. We have demonstrated a new method of fabricating textured ceramics with weak magnetic susceptibility by colloidal processing in a high magnetic field and subsequent heating [7]. The principle of this process is that a crystal with anisotropic magnetic susceptibility will rotate to the angle that minimizes the system energy when placed in a magnetic field. To obtain oriented materials with weak magnetic susceptibilities, the following conditions are necessary: (1) the crystal structure should be noncubic to yield anisotropic magnetic susceptibility, (2) the particle should be a single crystal and well dispersed, (3) the magnetic energy should be larger than the thermal motion energy, (4) the viscosity of the suspension should be sufficiently low for particles to rotate particularly upon applying a low energy, and (5) grain growth is necessary to obtain a highly oriented structure, especially when spherical particles are used. We have fabricated many types of oriented ceramics, including Al2O3, TiO2, ZnO, SiC, Si3N4, AlN, and their composites [7].

Electrophoretic deposition can be performed in a strong magnetic field. By changing the direction of the substrate relative to that of the magnetic field, we succeeded in fabricating oriented laminated ceramics [8], as shown in Fig. 8.

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**Fig. 8.** Electron backscatter diffraction (EBSD) map, SEM microstructure, and schematic diagram of textured laminated alumina prepared by EPD while changing the angle between the substrate and the applied magnetic field from 0° to 90° and vice versa.
Structural design

The objective of this project is to discover new functions of nanoceramics by controlling the local structure and composition at grain boundaries, the geometrical configuration and dimensional distribution of voids and crystal grains in the component phases, and other characteristics.

Fig. 9 shows an example where we aim to satisfy both superplasticity (a property enabling plastic molding such as that in metals at high temperatures) and high strength at room temperature to medium-to-high temperatures, at which the material will actually be used [9]. Ultrafine-grained densification with a grain size of \(<100\) nm has been realized using a tetragonal \(\text{ZrO}_2\)-\(\text{MgAl}_2\text{O}_4\) system through a crystallization/densification process involving the high-energy mixing of the raw material powders, resulting in the formation of an amorphous substance followed by spark plasma sintering. In addition to the fact that the bending strength increases to approximately double that of 3Y-TZP, superplasticity can be obtained at a high strain rate of \(10^{-2}\) s\(^{-1}\).

To create materials with such markedly enhanced multifunctional properties, design based on the elucidation of the local structure at grain boundaries and the state of existence of trace amounts of added cations will be indispensable. To achieve this, we are carrying out a
combined study of grain boundaries with various species of added cations, which includes the experimental analysis of high-temperature deformation, ionic conduction, and sintering; the high-resolution analysis of grain boundary structures; and a study of chemical bonding states using first-principles molecular orbit calculations [Fig. 10] [10]. By this, we hope to be able to elucidate the nanostructures at grain boundaries, the transport phenomena involved in both synthesis and properties, and the interrelationships of chemical bonding states to establish a foundation for the design of materials.

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