Review

Nano-structure Controls of Functional Powders

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Abstract

Recent developments in functional powders and their fabrication were overviewed with a focus on their microstructure and material design. We discuss features of four novel powders studied at Toyota CRDL: 1) Mono-dispersed super-microporous silica spheres, 2) Fullerene polymer-like materials, $C_{60}Pd_n$, for toluene adsorption, 3) Single-walled carbon nanotubes, and 4) Flame-synthesized metal oxides.

Keywords Powder, Synthesis, Microstructure, Material design

1. Introduction

Powders are used in various daily necessities including as ingredients in medical products, cosmetics, pigments, and other technologies. Typical examples are phosphor powders, which are essential in fluorescent lights, and fine carbon powder, which is required in rubber as a reinforcement material for automobile tires. Furthering the potential application of powder materials is the expectation that ultrafine particles with controlled structures will drastically raise their existing functional abilities and provide new functionality. To pursue this potential, the development of nano-scale particles has recently come under intensive study, e.g., researches on the synthesis and application of multi-walled, double-walled, and single-walled carbon nanotubes (CNTs). Applications of these nano-materials are expected in various fields including electronics and optics.

An ultrafine particle research project was undertaken as a national project of Japan in the 1980s. The National Nanotechnology Programs[1)] of the New Energy and Industrial Technology Development Organization have been in place since 2001.

Titania nanoparticles have been applied as photocatalysts and are also considered as candidate materials for solar cell components. Toyota CRDL developed the material which extended the phtocatalyst activity to visible-light wavelengths,[2)] and the potential applications of these nanoparticles include environmental preservation, such as in antibacterial and contamination control.

Research has been expanded to metal nanoparticles with unique characteristics. Sintering is remarkably promoted for nano-sized particles even at low temperatures, and in the case of silver nanoparticles, it was reported[3)] that metallurgical bonding between silver nanoparticles and a copper disc was completed at 280 ^{o}C under a pressure of 10 MPa. Silver nanoparticles are considered to be a leading candidate for replacing existing high melting point solder materials and would replace lead, an environmentally toxic substance, in solder junctions.

Mesoporous materials are the best examples of structure-controlled materials on the nano-scale. Since mesoporous silica was first reported[4)] in 1990, various types of mesoporous substances have been developed for metals, metal oxides, and organic-inorganic hybrid materials,[5)] and a very big research domain has been established based on them. Many applications are expected in various fields such as catalysis, adsorption, electricity, magnetism, and optical functions.

In this article, the methods of producing nano-scale functional powders are reviewed, and four research topics under investigation in Toyota CRDL are briefly mentioned. The methods of producing powders are categorized roughly into a solid-state reaction method, a liquid phase reaction method, and a gas phase reaction method. Generally, nanoparticles are formed only by a liquid phase reaction method or a gas phase reaction method. As for the solid-state reaction method, in contrast to other treatments, grain growth takes place during the high temperature treatment, and generally a nanoparticle cannot be obtained. A new technology, however, has been developed to break a coarse powder into even down to nano-scale particles using fine pulverizing media. The nanoparticles made by this technology are thought to be cost-effective.

2. Powders from liquid phase

The liquid phase reaction of soluble metal salts and/or metal alcoxides is utilized to precipitate a nano-scale solid particle. Various methods including the chemical precipitation method and the sol-gel method have been developed. Since two or more ingredients in the solution are intimately mixed, this method is advantageous to produce complex oxides with high homogeneity of the ingredients. Details of the synthesis methods are reported elsewhere.[6)]

Among the liquid phase reaction methods, the organic molecule templating method has been intensively studied in recent years in the fabrication of self-assembled mesoporous substances. The first technical article of this special issue deals with the mono-dispersed super-microporous silica spheres[7)]; the particle size of the silica spheres was precise1y contro11ed with their monodispersity maintained. The silica spheres in this study have a particle diameter equivalent to the wavelength of visible-light and thus application in optics as photonic crystals, for example, is expected.

The second technical article reports the characterization of $C_{60}Pd_n$ fullerene polymer-like material and its application as an adsorbent. This material was found to adsorb toluene, which is one of the most difficult volatile organic compounds to adsorb at room temperature without any additional energy. The theoretical study included in the article reveals that the overlapping of orbitals of π-electrons of both toluene and C_{60} stabilize this adsorption through the *d*-electron orbitals of the palladium atom.

3. Powders from gas phase

Gas phase reaction methods consist of chemical vapor deposition (CVD) and physical vapor deposition (PVD). Characteristic fine particles and thin films can be fabricated by gas phase reactions depending on the raw materials and heating methods, which include resistance heating, induction heating, a plasma method, a laser method, and a flame method. Since the synthetic atmosphere is controllable by the gas flow etc., not only oxides but also non-oxide particles can be produced. The research trends for nanoparticle synthesis by this method look towards the control of nano-structure and the formation of composite particles.

In the synthesis of CNTs, the CVD method enables structure control by selection of both the source gas and use of a catalyst. The ultimate nano-structure control for CNT will be to shape its chirality, which determines its conducting characteristic: metallic or semiconductive.

The third technical article reports the fabrication of single-walled CNTs by the CVD method using a catalyst.[8)] The techniques have been gradually improved to control the diameter and the number of walls of the CNT. A selective growth model for single-walled CNTs is proposed by considering competition between deposition and etching of the carbon atoms.

Flame synthesis is known as a method for producing huge amounts of colloidal silica or titania nanoparticles. Generally, the nanoparticles produced by this method are connected to one another in the shape of a rosary, and each particle is mostly spherical reflecting the condensation process from the gas phase. Forming complex particles on the nano-scale is one of the most interesting research targets for flame synthesis.

In the final technical article, this technique is applied to metal oxide nanoparticles.[9)] By clarifying the evolution process of the particles, their fine structure is expected to become controllable to achieve desirable properties.

4. Conclusion

It is usually thought that a new property must be obtained by realizing a novel particle structure or an alternative material composition. This is not always true. There are good examples where excellent nano-materials were obtained by deeply reconsidering the nature of known materials. One is the $12CaO\cdot 7Al_2O_3$ crystal, which is a well-known component of cement and had not been considered conventionally as a functional material at all. This substance, however, is a nanoporous crystal that consists of an atomic cage about 4Å in diameter and is a typical insulator. What was found recently[10)] is that, when it is exposed to ultraviolet light after the incorporation of H^- ions into the cages, the substance converts from an insulator into a persistent electronic conductor.

Another example does not involve a particle but the formation of a nano-scale functional surface layer.[11)] A silica fiber with a titania surface layer with a nano-scale compositional gradient was produced from a polymer precursor. In this process, the bleed-out phenomenon was effectively utilized to form the surface layer, whereas the phenomenon was conventionally understood as an undesirable degradation of the polymer material. This achievement must have been attained by analyzing the phenomenon in detail. The resultant understanding leads to the thinking that the undesirable property of the material is sometimes effectively available to the other one.

These successes teach us that a new function can be discovered not only by designing a new material, but by improving a known material. The importance of observing a substance from many aspects should not be overlooked.

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