Nanoparticle Preparation and Its Application
- A Nanotechnology Particle Project in Japan

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Abstract

Nanoparticles such as metals, semiconductors and metal oxides are of great interest for a wide variety of applications in the field of information, energy, environmental and medical technologies due to their unique or improved properties determined primarily by size, composition and structure along with their self-organized film structures. In this presentation, Japan's national project on nanoparticle synthesis and its applications in nanotechnology programs is reviewed along with some new findings on synthesis technologies and the related nanoparticle-based nanostructures developed during the project. The synthesis methods include liquid phase, gas phase, liquid-based gas phase such as novel spray methods and sol-gel assisted in-situ techniques and continuous mass production method.

1. Introduction

Nano-sized particles ranging below several 10 nm are of great interest, because of the chemical and physical behavior of the particles arising from the quantum size effect which are remarkably different from those in bulk form giving the great potential for use in applications in the electronic, chemical and mechanical industries, as well as in the related technologies using catalysts, drug carriers, sensors, pigments, also as well as in magnetic and electronic materials.

The usage of the unagglomerated particles with sharp size distribution is preferred for practical applications and technologies, especially for compacting or self-arranging the particles. A number of techniques for the preparations of nanoparticles that satisfy this requirement have been developed via gas and liquid phase processes. To be industrially relevant, the process needs to be low-cost and involve both continuous operation and a high production rate.

In this presentation, a national project on nanoparticles funded by the Japanese government will be introduced followed by the explanation of the outline on the synthesis of nanoparticles via gas and liquid processes and nanoparticle-based nanostructured materials investigated through this project [1]. The model materials used include: noble metals, magnets, phosphors, and luminescent semi-conductor materials. Some novel techniques for preparing nanoparticles focusing especially on controlling the agglomeration were developed.

2. Nanoparticle Project in Japan

The Nanotechnology Particle Project (2001–2005, with K. Okuyama as project director) has being conducted as a part of the "Nanotechnology Materials Program" funded by the METI through the New Energy and Industrial Technology Development Organization (NEDO). The objective of the Nanotechnology Particle Project is to establish a platform for developing the synthesis and functionalization technologies of nanoparticles, which is important for producing nanostructures and expressing nano-functions imparted as quantum size effect. Through the expression of chemical, electronic, magnetic, optical and mechanical properties that are totally different from

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the same material in bulk form, it is possible to create a new system of materials technologies that can be used in a wide range of application fields, including chemistry, electronics, magnetics, electrical engineering, optics, catalysts, ceramics, and mechanics. In this project, the following research fields will be carried out; (1) research and development of high-rate synthesis technology for single-nanometer sized nanoparticles; (2) research and development of surface modification and the nanoparticles self-organized thin film fabrication technologies; (3) preparation and performance evaluation of the device elements utilizing nanoparticles, and (4) systematization of related technologies.

In the synthesis of nanoparticles, liquid phase synthesis (e.g., micro-emulsion, reverse micelle process, hot-soap process, spray pyrolysis) and gas-phase synthesis will be conducted to elucidate the particular features of the various methods by investigating particle diameter, particle size distribution, morphology/shape, surface characteristics, compatibility with materials and their link with the surface modification techniques.

Measurement techniques are being developed for in situ and precise-detection of the nucleation and coagulation growth process of single-nanometer sized particles. Based on these considerations, synthesis methods are then developed for nanoparticles used in model materials.

3. Nanoparticle Synthesis

3.1 Preparation of Metal Nanoparticles

There are various liquid phase methods for preparing nanoparticles such as the chemical reduction, sol-gel, reversed micelle, hot-soap, pyrolysis, and spray pyrolysis methods. Noble metal nanoparticles with spherical shape and sharp size distribution such as Au were produced continuously by the chemical reduction method assisted by ultrasonic device. By changing the amount of tannin acid into the mixture of $AuCl_4H$ and sodium citrate dihydrate, particle diameter of Au nanoparticles can be controlled between 5 and 17nm. The monodispersed Ag nanoparticles ranging below 10nm in diameter have been obtained in more than 100mM of Ag concentration of precursor liquid. These colloidal metal nanoparticles have many applications in electronics, such as, interconnection materials and in catalysis.

3.2 Preparation of Magnetic Nanoparticles

It was predicted that using magnetic nanoparticles approximately 3 nm in size, which contain hundreds of atoms, one could make recording media of up to 1 Tb/in^2 in recording density, by correctly organizing the particles. FePt nanoparticles are candidate for developing ultra high density magnetic media. The FePt nanoparticles have been synthesized by mixing two precursor liquids: ferric acetyl acetonate, $Fe(acac)_3$, and platinum acetyl acetonate, $Pt(acac)_2$ in polyol solution of sodium hydroxide at high temperatures[2]. The particle size distribution was monodisperse and the morphology was none agglomerating. Magnetic evaluation of samples annealed at high temperature indicated the high coercivity values close to 10 kOe at room temperature, even though the size of the particle is as low as a single nanometer (below 10 nm). The mass production of FePt nanoparticles has been performed by the continuous mixing method. The FePt nanoparticles have also many applications such as catalyst for fuel cells, drag delivery systems (DDS) and biosensors.

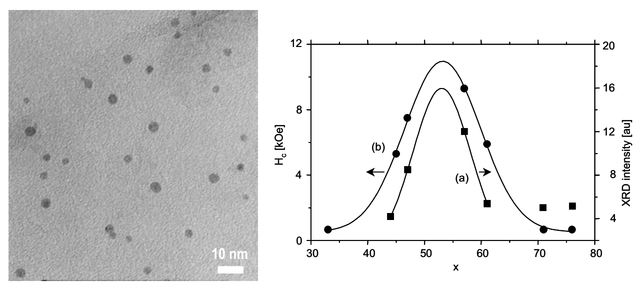

Figure 1. Left:: Polyol-Process-made Fe-Pt Particles (After Annealed). Right:: Effect of Fe-Fraction on the Coercivity and Crystallinity.

3.3 Preparation of Luminescent Nanoparticles (Quantum Dots)

Phosphor nanoparticles of CdSe/ZnS (core/shell) were synthesized using a continuous hot-soap reactor as well as a batch process [3]. The emission luminescence wavelength of the nanoparticles prepared by the continuous route has a somewhat wider spectrum than those prepared by the batch route. However, the continuous process showed the possibility of fabricating the luminescent semiconductor nanoparticles, in which the luminescent spectra can be controlled from the range of blue to red depending on the particle size.

3.4 Chemical Vapor Deposition (CVD) and Control of Particle Agglomeration

Chemical vapor deposition (CVD) is one of the commonly used gas-phase aerosol processes for producing high-purity nanoparticles though generated nanoparticles are in the form of aggregates due to their coagulation at the high temperatures used. Non-agglomerated spherical oxide (SiO_2, TiO_2, ZrO_2) nanoparticles having diameters in the range of 10–40 nm has been prepared using an electrospray assisted chemical vapor deposition (ES-CVD) technique[4]. ES-CVD represents a method that can be used to control the size and morphology of synthesized particles in gas-to-particle conversion processes.

3.5 Preparation of via Spray Route

Spray pyrolysis is a liquid-based gas phase method and electrospray is capable of generating fine droplets as well as nanoparticles. We report a novel synthesis route by spray pyrolysis (salt-assisted spray pyrolysis (SASP)) for the continuous synthesis of nanoparticles with adjustable sizes, a narrow size distribution, high crystallinity, and good stoichiometry[5]. In this method, many kinds of single crystalline nanoparticles (oxide; Y_2O_3-ZrO_3, CeO_2, NiO, Eu doped Y_2O_3, ZnO, Ba-Sr-Ti-O, Mn doped ZnS, metal; Ag-Pd) can be prepared (Fig. 2). This route can offer good controllability of particle size, chemical composition, and material crystallinity, all of which are important for advanced materials.

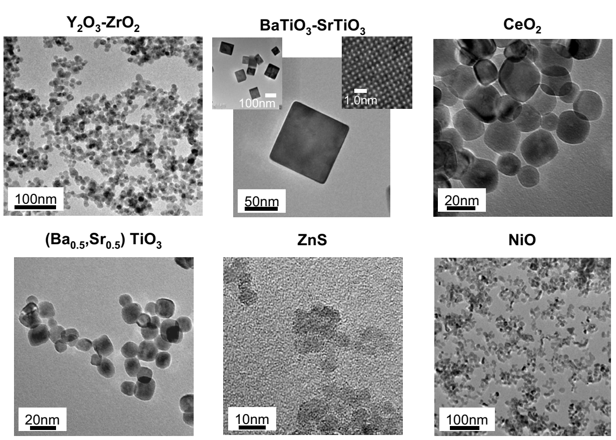

Figure 2. Nanoparticles Prepared by SASP

4. Particle-based Nanostructured Materials

4.1 Self-organized Porous Particles

The synthesis of meso-structured porous materials represents a fascinating and intellectually challenging problem due to its potential for applications in catalysts, chromatography, and the controlled release of drugs, microelectronics, and electro-optics. A colloidal mixture of silica nanoparticles and polystyrene (PS) latex nanoparticles was sprayed as droplets into a vertical reactor equipped with several temperature zones. The PS nanoparticles in the powder were decomposed in the reactor to produce a silica powder consisting of mesopores. The mesopores were observed arranging into a hexagonal packing, indicating the self-organization process occurred spontaneously during solvent evaporation. The entire process was completed in only several seconds, which is far more accelerated compared to current methods.

4.2 Nanoparticle-assisted Photonic Crystal

Materials with three-dimensional (3D) periodic structures have been the subject of considerable attention from theorists and experimentalists for the application of photonic crystals, advanced coatings, advanced catalysts and many other functional materials.

The preparation procedure is close to the above route for producing silica films containing ordered porous silica films, with pore sizes in the range of 40–1000 nm[6]. This method permits the pore size to be selected by appropriate adjusting of the size of the PSL particles.

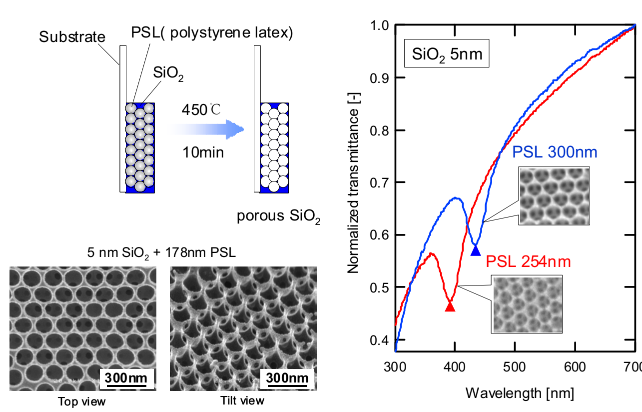

Figure 3. Photonic Crystals

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The 3D ordered porous films prepared by the present method provide the optical band gap materials which is dependent on the dielectric constant periodicity of the material.

4.3 Nanoparticle-based Polymer Electrolyte

A new preparation method for producing highly conductive polymer electrolytes has been investigated using nanoparticles as luminescent centers. The ZnO nanoparticles were grown in a polymer electrolyte, producing nanoparticle-loaded polymer electrolytes in a one-step process. This approach ensures the dispersion of nanoparticles in the polymer bulk easily without the need for an intensive mixing process. By this method produced the composites phosphor having colors ranging from blue to almost yellow.

From the luminescent spectrum ZnO polymer electrolyte doped with europium (Eu) gives the red color[7]as is shown in Fig. 4A where ZnO-Eu/Polymer composites prepared at various LiOH concentrations with excited at wavelengths coinciding with either the exciton peak or bandgap peak of the ZnO. Fig. 4B displays the emission spectra of ZnO-Eu/Polymer composites using excited wavelengths coinciding with the peak $^7F_0 \rightarrow ^5D_6$ transition. This produces a high emission intensity at 616nm and relatively low intensity at 594nm. We have also prepared luminescent polymer electrolyte composites where the luminescent spectrum varies from blue to red in color.

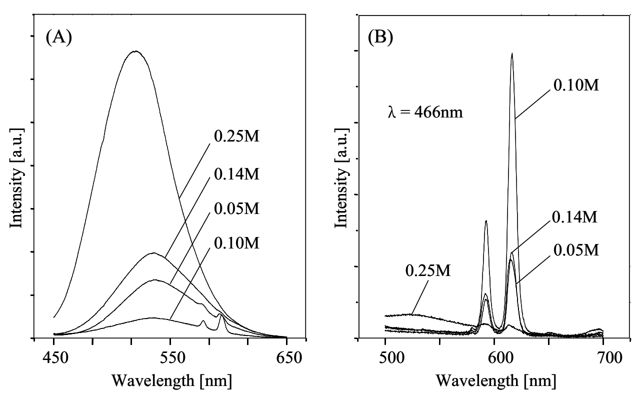

Figure. 4 Luminescence of ZnO-Eu/PEG Prepared with Various LiOH Concentrations with Excited (A) Wavelengths Coinciding with the Bandgap Peak of ZnO and (B) 466nm.

5. Conclusions and Future Work

A number of nanoparticles-related research projects are actively being conducted in several countries. To establish a good correlation between nanoparticles and particle-based nanostructures or devices, it is necessary to secure human resources with a systematical organization, e.g. a national project. To put the research results of the wide variety of nanoparticles to practical use it is very essential to establish technology for measuring and evaluating the characteristics and performance of nanoparticles and nanostructures. Research and development of high-rate synthesis technology for nanoparticles also depend on the evaluation of particle generation in the liquid and gas-phases examined experimentally and on the design of the reactor made by the use of a numerical simulation.

Acknowledgments

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