Supercritical Hydrothermal Synthesis of Organic Inorganic Bomolecule Hybrid Nano Particles

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Summary

We have proposed and developed a method of supercritical hydrothermal synthesis of metal oxide nanoparticles. Recently, we modified this new method to synthesize organic-inorganic-bio-molecule fused materials. By introducing organic species (aminoacids, carboxylic acids, amines, alcohols, aldehydes etc.) during supercritical hydrothermal synthesis, nanoparticles whose surface was modified with organic materials were synthesized, which was probably due to the homogeneous phase formation in supercritical conditions. We succeed in synthesizing surface modified metal oxide nanoparticles (several to 20 nm), which cannot be synthesized by the other methods. Modification of bio-materials including amino acids or peptides is also possible. This type of surface modification allows the designer to incorporate unique characteristics of the nanoparticles into their products, including perfect dispersion of inorganic nanoparticles in aqueous solutions, organic solvents or in polymers. This can be used for nanohybrid polymers, nano-ink, or nano-paints. Furthermore, bio-modification of nanoparticles leads to form nanobiohybrid materials.

Introduction

Nanotechnology for control of material structures to the nanometer scale (0.1 to 100 nm) will be a necessary platform for future industries. The density of transistors on a chip has roughly doubled every eighteen months over these 10 years (Moore's law) and now with the semiconductor industry entering the "90 nm node" era with actual gate lengths being 50 nm, new fabrication methods will be necessary. Besides the semiconductor industry, materials including nanoparticles will find applications in areas, such as suntan lotions, cosmetics containing ultraviolet-absorbing nanoparticles, organic solar cells, anti-corrosion coatings, photocatalytic air purifiers, longer-lasting medical implants1. Nanostructured materials will be used for nanoelectronic components based on quantum effects such as superparamagenetism, plastic electronics and flat panel displays, high-density memories, or for medical fields, such as a drug delivery system, biochip arrays for a powerful diagnostics1.

For nano- particles or fiber synthesis, various approaches have been introduced including reverse-micelle, hot soap, spray decomposition, gel-sol method (inhibition of nanoparticle coagulation), and supercritical synthesis, where in-situ surface stabilization is a key to synthesize nanoparticles. Furthermore, control of surface characteristics through surface reactions with organic molecules, further with biomolecules, is also tried for exploring the synthesis of hybrid materials, and programmed assembly of nanoparticles.

In this paper, we will describe in situ surface modification of nanoparticles in sub-critical and supercritical conditions from 473 K to 673 K during supercritical hydrothermal synthesis (Adschiri et al. 1992, 2001, 2003, and Hatakeyama et al, 2004). Because of the formation of

homogeneous reaction atmosphere for organic modifiers and high temeprature water, organic-inorganic reactions successfully proceed to form organic-inorganic hybrid nano particles.

Experimental

2.1 Reagents

Pressure-resistant tube reactors (SUS 316) whose inner volume was 5.0 mL were used for hydrothermal synthesis. The reactor was loaded with 2.5 mL of 0.1M of metal salt aqueous solution. In order to modify the surface of metal oxide nanoparticles, 0.1 mL of the surface modifier was added. Surface modifiers were alcohols, aldehyde, carboxylic acids, amines, thiols, and alginic acid, and obtained from Wako Chemicals Ltd. The reactors were then capped tightly and put in an electric furnace whose temperature was maintained at 200, 300 and 400°C. The reaction was performed for 10 min and terminated by quenching the reactor in a water bath. After quenched, the reactor was washed by distilled water and isooctane in turn to collect solid products. The obtained products were purified by three cycles of a combination of decantation and centrifugation using ethanol. Then similar procedure was performed twice using distilled water. Finally, the products were purified by X-ray diffraction (XRD) measurement. The size and shape of the nanoparticles were studied by using the transmission electron microscopy (TEM, JEM-1200 EXII (JEOL, Ltd.)). The chemical bonds on the surface of products were evaluated by Fourier transform infrared spectroscopy (FTIR).

RESULTS AND DISCUSSION

First, a series of experiments was conducted to examine reactions of modifiers and metal oxide Particles were loaded in a 5 ml of surface. autoclave with a surface modifier (0.1 ml) and water (2.5 ml.). The reactor was heated up to 473, 573 or 673 K and kept at the temperature for 10 min. The products were recovered in two phase solvents of water and chloroform. Figure 1 shows the results of hexanal treatment for TiO₂ at 673 K. As shown in this figure, original particles were dispersed in a water phase, but organic treated particles were dispersed in a chloroform phase. This suggests that the surface of TiO₂ were modified with organic molecules during the treatment in high temperature By the FTIR analysis, we confirmed the water. organic were chemically bonded on the surface of TiO₂, which will be discussed later.



Figure 1. Control of hydrophobic and hydrophilic interaction by modification of TiO_2 nanoparticles in supercritical state.

Next, in-situ surface modification experiments were conducted. For the experiments of Co_3O_4 , particle size was compared for with and without a modifier, hexylamine. The average size of the nanoparticles was (a) 50 nm for products without modifier and (b) 20 nm for products with the modifier. We also notice that (a) the nanoparticles synthesized without modifier have their own particular crystalline structure while (b) nanoparticles with modifier have spherical shape, for the case of Co_3O_4 . These results indicate that the modifier attached on growing surfaces of the nanoparticles and changed their energetic stability that closely relates to the size and crystalline structure of nanocrystals.

Figure 2 shows a TEM image of Fe_2O_3 nanoparticles treated with dodecanylacid in in-situ reaction experiments. As show here, around 10-20 nano meter size of particles could be obtained. Particle size distribution was very narrow and the phaset could be observed even for these nano size particles, which implies formation of single crystal. TEM results also

implies that using the modifiers can prevent from agglomeration between cobalt oxides nanoparticles and the size of particles decreases as well as temperature increases.

FTIR analysis was used for investigation of formed bonds between nanoparticles and modifiers. Figure 3 shows FTIR spectra for dodecanylacid treatment on Fe₂O₃. As shown in this figure, peaks of CH₂ and CO functional groups could be observed. This clearly indicates the formation of chemical bonds between the surface of metal oxide and organic molecules. Also for the other modifiers and metal oxides, chemical bond formation was observed, although the conditions were different among the systems.

It was also confirmed that amino acids (alginic acid) modification of metal oxide nanoparticles was possible. According to the results of the experiments of amine and carboxylic acid, amino functional group of alginic acid may react with hydroxyl groups of metal oxide surface.

Once the surface is covered with the organic chemicals, bio-molecules can be combined with onto them. Bio-modification of nanoparticles leads to form nanobiohybrid materials. Figure 4 shows the results of addressing the DNA modified nanoparticles onto the self-assembled DNAs. Six kinds of single strand DNAs were designed to self-assemble each other to make ladder like structures, side of which has single strand DNAs. Gold nanoparticles were modified with single strand DNA which is complementary with the single strand DNA on the side of the ladder like structure.

Figure 5 shows addressing the protein *EcoR*I modified nanoparticles on to DNA. *EcoR*I is an enzyme to cut DNA on the base arrangement shown in this figure. However, in the absence of Mg ion, *EcoR*I does not cut DNA but just attached to the position. In this study, Gold nanoparticles were modified with *EcoRI* and then placed onto the DNA in the absence of Mg ion, as shown in this figure,

In high temperature water, amino acids are dehydrated to form peptides, which are selfassembled together to make large morphologies. Compared with a surfactant which has both hydrophobic and hydrophilic functional groups, protein can have hydrophobic-hydrophilic plus positive-negative natures SO that various morphologies are possible such as micelles, tubes, films. This can be used as a substrate for combining with bio-modified nanoparticles. Thus, tunable reaction atmosphere and solvent properties of supercritical fluids provide various possibilities for



Figure 2. TEM image of carboxylic acid modified Fe_2O_3 .



Figure 3. FTIR Analysis of the surface modified nanoparticles



Figure 4. Programmed assembly of Nanogold particles with DNAs.



Figure 5. Addressing peptide nanoparticle conjugate

nanotechnology and nano-biotechnology. This kind of bio-modification of nano particles paves a way to the programmed assembly of nanoparticles for the fabrication of IT devices.

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