We propose a new method to synthesize organic-inorganic hybrid nanoparticles using supercritical hydrothermal synthesis. By introducing organic species (aminoacids, carboxylic acids, amines, alcohols, aldehydes etc.) during supercritical hydrothermal synthesis, nanoparticles whose surface was modified with organic molecules were synthesized. This is probably due to the homogeneous phase formation in supercritical conditions. Particle size was in the range from several to 20 nm. By selecting a proper surface modifier, particles could be dispersed perfectly in organic solvent or in aqueous solutions. This implies a variety of applications of the nanoparticles including nanohybrid polymers, nano-ink, and nanopaints.

1. Introduction

Nanotechnology for controlling material structures of the nanometer scale (0.1 to 100 nm) will be an important technology platform for future industries. For semiconductor industries, the density of transistors on a chip has roughly doubled every eighteen months over these 10 years (Moore’s law) and now the semiconductor industry has entered the "90 nm node" era with actual gate lengths being 50 nm, for which the present lithography method using UV light encounters the difficulty in fabrication of integrated circuit chip. Thus, so-called bottom-up technology to build up nano-structures from nanoparticles will be necessary. For the other industries, 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 implants. Nanostructured materials will be used for nanoelectronic components based on quantum effects such as superparamagnetism, plastic electronics and flat panel displays, high-density memories, or for medical fields, such as a drug delivery system, biochip arrays for a powerful diagnostics [1].

For nano-particles or fiber synthesis, various approaches have been developed including reverse-micelle, hot soap, spray decomposition, gel-sol method, and supercritical hydrothermal synthesis [2-4]. In these methods, control of surface characteristics is a key to stabilize nanoparticles (inhibition of aggregation of nanoparticles). Surface modification of nanoparticles with organic molecules, further with biomolecules, is essential to synthesize hybrid materials, and programmed assembly of nanoparticles [5].

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. Because of the formation of homogeneous reaction atmosphere for organic
modifiers and high temperature water, organic-inorganic reactions successfully proceed to form organic-inorganic hybrid nanoparticles.

2. Experimental

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 crystallographic identity of the solid products was identified 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).

3. Results and Discussion

First, a series of experiments was conducted to examine reactions of modifiers and metal oxide surface. TiO₂ nanoparticles were loaded in a 5 ml of autoclave with a surface modifier (0.1 ml) and water (2.5 ml). The reactor was heated up to 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 water. By the FTIR analysis, we confirmed the organic were chemically bonded on the surface of TiO₂, which will be discussed later.

Next, in-situ surface modification during hydrothermal synthesis was conducted. Figure 2 shows a TEM image of Fe₂O₃ nanoparticles treated with dodecanylacid. 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. Crystalline size evaluated from XRD peaks was more or less the same as the particle size observed by TEM. These results indicate the formation of single crystal. TEM results also imply that the modifiers can prevent from aggregation of nanoparticles and the size of particles decreases as well as temperature increases. This is probably because the modifier attached on growing surfaces of the particles suppressed the particle growth.

By selecting a proper surface modifier, particles could be well dispersed in organic solvents or in water. Thus, as shown in Figure 3, transparent solution-like products could be obtained. Since the particle size is much smaller than the wave length of visible light, if the
particles are not aggregated and well dispersed in solvents, the suspension should be transparent like in Figure 3. Thus, the results suggest a perfect dispersion of nanoparticles in these solvents. Perfect dispersion of nanoparticles in organic solvents or in water allows us to apply the nanoparticles for manufacturing nanohybrid polymers, nano-ink, or nano-paints.

FTIR analysis was used for investigation of formed bonds between nanoparticles and modifiers. For the case of dodecanylacid treatment on Fe_2O_3, peaks of CH_2 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.

Although the mechanism of surface modification in hydrothermal synthesis has not yet been elucidated, at the moment we think, it is as shown in Figure 4. During the hydrothermal synthesis, metal oxide surface should be covered by hydroxyl functional group, which can react with alcohol, carboxylic acids, amines, aldehydes etc. probably through dehydration. It is important that these organic surface modifiers are miscible with aqueous solutions, under supercritical or subcritical conditions.
4. Conclusion

We proposed a new method to synthesize organic-inorganic hybrid nanoparticles using supercritical hydrothermal synthesis. 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. By the in-situ surface modification smaller particles could be obtained, which is probably due to the suppression of particle growth by the capping effect of the modifiers. The surface modified particles could be well dispersed in organic solvents or in water, by controlling the surface modifiers.

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5. References