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Supercritical hydrothermal synthesis of organic-inorganic hybrid nanoparticles

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Abstract We have developed supercritical hydrothermal synthesis method of metal oxide nanoparticles where metal salt aqueous solution is mixed with high temperature water to rapidly increase the temperature of the metal salt solution and thus reduce the reactions and crystallizations during the heating up period. By using this method, we succeeded in the continuous and rapid production of metal oxide nanocrystals.

A new method proposes to synthesize organic-inorganic fused materials based on the methods of supercritical hydrothermal synthesis. By introducing organic materials in a reaction atmosphere of supercritical hydrothermal synthesis, we successfully synthesized metal oxide nanoparticles whose surface was modified with organic materials. In supercritical state, water and organic materials form a homogeneous phase, which provides an excellent reaction atmosphere for the organic modification of nanoparticles. Modification with bio-materials including amino acids was also possible. By changing organic modifiers, particle morphology and crystal structure were changed.

This organic surface modification provides a various unique characteristics for the nanoparticles: Dispersion of nanoparticles in aqueous solutions, organic solvents or in liquid polymers can be controlled by selecting hydrophilic or hydrophobic modifiers.

1. Introduction

Nanotechnology is defined as a technology to use materials whose dimension is in the range from 0.1 to 100 nm and thus physical and chemical properties are different from bulk one. Nanoparticles are considered as essential materials in nanotechnology. Physical and chemical properties of nanoparticles can be varied by changing size and morphology of the nanoparticles. Especially the size of the particles reflects in the increase in the ratio of surface to volume as surface or interface induced effect. The size effect, in particular the quantum size, is mainly considered to describe physical properties (the quantum size effect appears where the normal bulk electronic structure is replaced by a series of discrete electronic levels). While the surface or interface induced effect plays an important role for chemical processing [1]. For example, the increase in the performance of catalysis and structures such as electrodes for the improvement of such technologies as fuel cells and batteries is because of the surface or interface induced effect. However in the size effect, when the size of nanoparticles is lower than critical wavelength of light (less than 100 nm), a useful property as transparent which can be applied in packaging, cosmetics and coating will be appeared [2]. In biotechnology, labeling of cell by fluorescent nanoparticles and hyperthermia with magnetic nanoparticles are interested for applications of nanoparticles in biomedical aspects [1].

Production of nanoparticles can be carried out by chemical and physical methods. We proposed an original method of supercritical hydrothermal synthesis to produce nanoparticles [3–5]. Conventional hydrothermal synthesis of metal oxides from aqueous solutions is typically utilized at temperature ranging from 373 K to 473 K and in a batch-type autoclave reactor. In the proposed method with a flow type tubular reactor, metal salt aqueous solution was mixed with high temperature water to increase the solution temperature rapidly up to the supercritical state. Because of the high reaction rate of hydrothermal

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synthesis and low solubility of metal oxides, extremely high super saturation degree is attained just after the mixing point. This leads to the formation of nano meter size particles [3–5].

Successful application of nanoparticles includes using inorganic nanoparticles as filler in polymers to improve barrier properties, electrical conductivity and refractive index depends on their proper disperse into the fluids [6]. However, metal oxide nanoparticles produced in a water phase, due to the presence of hydroxyl groups on their surface, can not easily be dispersed in a non-polar organic material, unless a dispersing agent is used. A proper surface modifier can prevent particle growth and the surface modification of nanoparticles improves dispersion property as well as chemical, electrochemical resistance and optical appearance properties [6]. If metal oxides can be modified very well, a large number of new or improved engineering products can be produced. Furthermore, once the nanoparticles are modified with amino acids, peptides, proteins, or DNA, the particles can be specifically combined with other proteins or DNA, which leads to the applications to new biotechnology or IT devices using programmed assembly of semiconductor nanoparticles.

There are some methods for surface modification of metal oxide particles, including silane coupling for surface modification of oxides. In silane coupling, the metal oxides must be dipped into an organic solution. Since the surface of metal oxide nanoparticles is surrounded by hydroxyl groups (hydrophilic), they can't easily be dispersed in that solution for surface modification. Another method as CNBr activation can't be used for surface modification because the reaction media is acidic and can dissolve metal oxide nanoparticles [7]. Thus, these methods can't be used as suitable manner for surface modification of metal oxide nanoparticles.

In this paper, we will describe in situ surface modification of nanoparticles in sub-critical and supercritical conditions at 200, 300 and 400°C by hydrothermal synthesis as an attractive method for production of metal oxide nanoparticles. 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. We used various kinds of organic modifier and metal oxides systems.

2. Experimental

2.1. Reagents

$Al(NO_3)_3$, $Ce(NO_3)_3$, $CoSO_4$, $Fe(NO_3)_3$, $FeSO_4$, $Ni(NO_3)_2$, $Ti(SO_4)_2$, $Zn(NO_3)$, and $Zr(NO_3)_4$ were used as starting materials in this study and were purchased from Wako Chemicals Ltd. CeO_2, CO_2O_3, Fe_2O_3, NiO, SiO_2, SnO_2, TiO_2, and ZnO particles purchased from Wako Chemicals were also used. Surface modifiers used were alcohols, aldhydes, carboxylic acids, amines, thriols with C6, C8 and C10 hydrocarbons and alginic acid, which were from Wako Chemicals Ltd. Water was distilled by EYELA STILL ACE SA-2100E and used for hydrothermal synthesis.

2.2. Hydrothermal synthesis and surface modification in subcritical and supercritical water

Pressure-resistant tube reactors (SUS 316) whose inner volume was 5.0 mL were used for hydrothermal synthesis with in-situ surface modification. The reactor was loaded with 2.5 mL of 0.1 M of metal salt aqueous solution. In order to modify the surface of metal oxide nanoparticles, 0.1 mL of the surface modifier was added. The reactors were then capped tightly and put in an electric furnace whose temperature was maintained at 200, 300 or 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 with ethanol and dried.

2.3. Characterization

The crystallographic identity of the solid products was evaluated 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 seris of experiments was conducted to examine reactions of modifiers and metal oxide surface. Particles were loaded in a 5 ml of autoclave with a surface mofidier (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. Fig. 1 shows the results of hexanal treatment for TiO_2 at 673 K. As shown in this photo, original particles were dispersed in a water phase, but organic treated particles were dispersed in a chloroform phase. This suggests that the surface of TiO^2 were modified with organic molecules during the treatment in high temperature water. By the FTIR analysis, we confirmed the hyxanal were chemically bonded on the surface of TiO_2, which will be discussed later.

Fig. 2 shows a TEM image of Fe_2O_3 nanoparticles obtained by in-situ reaction and modification experiment, namely hydrothermal synthesis with dodeconoic acid. As

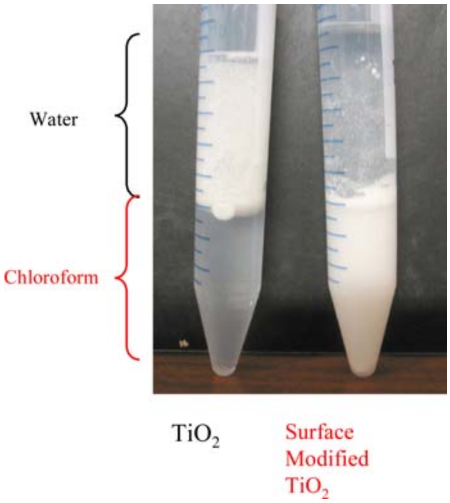

Figure 1 Control of dispersion of nano particles in water and organic solvent.

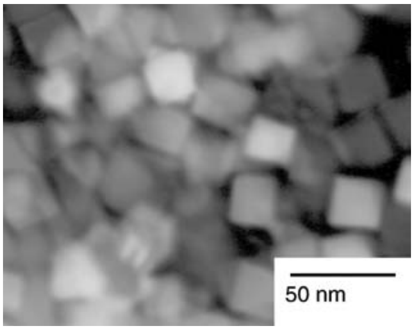

Figure 2 TEM image of decanoic acid modifed Fe_2O_3 nano particles

show here, around 10–20 nano meter size of particles could be obtained. Particle size distribution was very narrow and the facet could be observed even for these nano size particles, which implies formation of single crystal.

Fig. 3 shows XRD patterns of surface modified nanoparticles of cobalt oxide. Even for the nano meter size particles, relatively sharp peaks were obtained. This also suggests the high crystallinity of the obtained products.

For the experiments for CO_3O_4, particles, size were 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. It was observed in the case of CO_3O_4 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 to their energetic stability that closely relates to the size and crystalline structure of nanocrystals. 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 bands between nanoparticles and modifiers due to the chemical interaction. Fig. 4 shows an FTIR spectra for dodecanylacid treatment on Fe_2O_3. As shown in this figure, peaks of CH_2 and CO functional groups could be observed. This clearly indicates the formation of chemical bonding between the surface of metal oxide and docecanylacid. Also for the other modifiers and metal oxides, chemical bond formation was observed, although the conditions were different among the systems.

The process of reaction by these modifiers may be described as the following reactions:

$$\text{MO-(OH)}_X + \text{y(HO-R)} = \text{MO-(OH)}_{x-y}\ \text{y(O-R)} + \text{yH}_2\text{O} \quad (1)$$

$$\text{MO-(OH)}_x + \text{y(H}_2\text{N-R)} = \text{MO-(OH)}_{x-y}\ \text{y(H-N-R)} + \text{yH}_2\text{O} \quad (2)$$

$$\text{MO-(OH)}_x + \text{y(HC(O)-R)} = \text{MO-(OH)}_{x-y}\ \text{y(C(O)-R)} + \text{yH}_2\text{O} \quad (3)$$

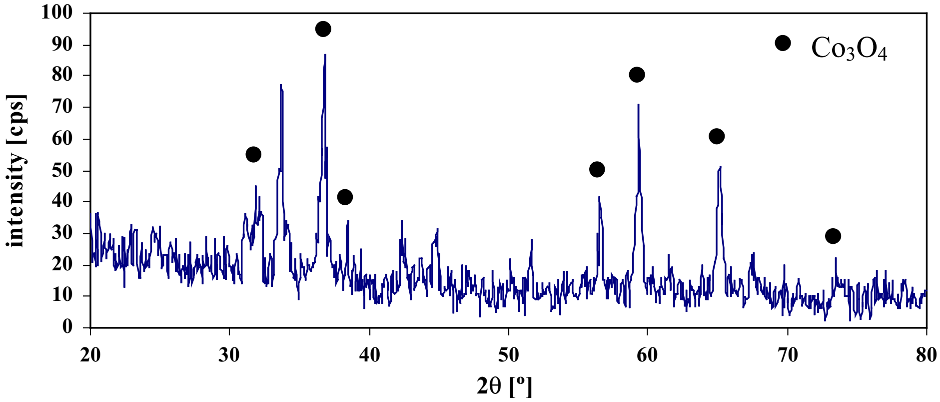

Figure 3 XRD patttern for hexanal modifed Co_3O_4.

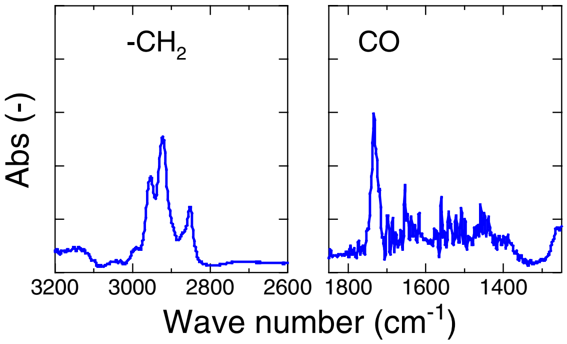

Figure 4 FTIR spectra of $C_9H_{19}COOH$ modified nanoparticles.

$$\mathrm{MO\text{-}(OH)_x + y(HOC(O)\text{-}R) = MO\text{-}(OH)_{x-y}} \\ \mathrm{y(OC(O) - R) + yH_2O} \qquad (4)$$

The optimum conditions for the surface modification differ among the modifiers and metal oxides. For the case of modification of cobalt oxides with hexyl functional groups, only C_5-CHO at 400°C and C_6-NH_2 at every temperature (200, 300 and 400°C) can modify the surface. But C_6-SH can't work for surface modification at 400°C. In spite of presence of some particles in organic phase, XRD showed that these products are some kind of cobalt sulfide compositions and there is not any cobalt oxide.

It was also confirmed that amino acids (alginic acid) modification of metal oxide nanoparticles was possible for iron oxide. 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. The amino acids modified nano particles look like polymer, rather than solid powders. This is probably due to self-assembly of nanoparticles through the specific interaction of amino group and carboxylic group on the surface of nanoparticles. This kind of bio-modification of nano particles paves a way to the programmed assembly of nanoparticles for the fubrications of IT devices.

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