

# SUPERCRITICAL HYDROTHERMAL SYNTHESIS OF ORGANIC HYBRID NANOPARTICLES -MECHANISTIC STUDY-

Tadafumi Adschiri\*

WPI Research Center:Advanced Institute for Materials Research (WPI-AIMR),

Tohoku University

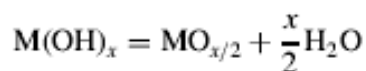
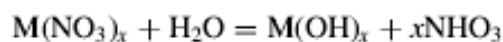
E-mail: ajiri@tagen.tohoku.ac.jp

We propose a new method to synthesize organic-inorganic hybrid nanoparticles at supercritical hydrothermal conditions. By introducing organic legends (aminoacids, carboxylic acids, amines, alcohols, aldehydes etc.) into supercritical hydrothermal synthesis atmosphere, organic -inorganic hybrid nanocrystals were synthesized. Particle size was in the range from 2.5 nm to 10 nm, and particle size dispersion was extremely narrow. Crystal shape can be controlled to be sphere, nano-cube etc. by changing concentration of organic modeifiers. By selecting a proper modifier (affinity with the solvent), particles could be dispersed perfectly in organic solvents or in aqueous solutions. This implies a variety of applications of the nanoparticles including nanohybrid polymers, nano-ink, nano-paints, and bio-imaging probe. In this paper, mechanism of the reaction was discussed. Important is homogeneous phase formation for the organic substance and metal salt aqueous solutions at supercritical conditions. Through the experiments of changing pH, it was found that the matching of surface charge of the nanoparticles and the dissociation of organic molecules under supercritical conditions was essential for the surface modification.

## INTRODUCTION

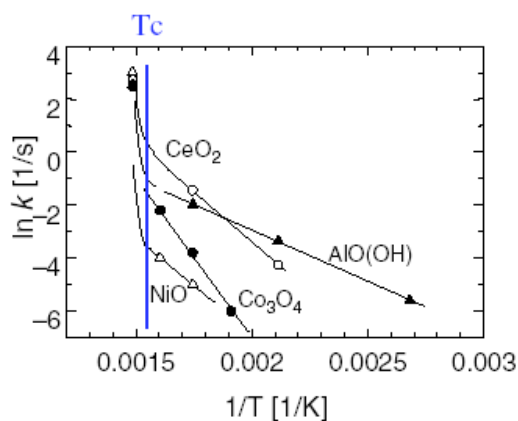
Metal oxide nanoparticles are expected to be used for variety of applications, including semiconductor materials, polymer hybrid materials, medical applications, transparent pigments, electro-magnetic materials, catalysts, and cosmetics. For all the cases, control of crystal structure, particle size, and morphology is essential.

Hydrothermal synthesis is a widely used method to synthesize metal oxide crystals from metal salt aqueous solution at elevated temperature around several 10–300 °C in a pressure-resistant vessel.

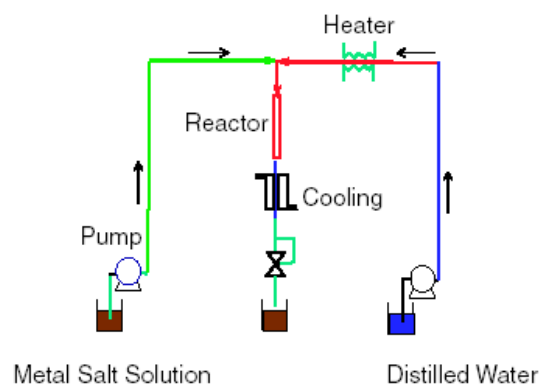


The metal oxides that have been synthesized by hydrothermal synthesis so far cover almost all the metal oxides over the periodic table, except alkaline metals that show high solubility in water. However, nanocrystals have not always been synthesized by the conventional methods, since crystal grows by Ostwald ripening mechanism in high-temperature water.

We proposed a method to synthesize nanometer size metal oxide rapidly and continuously at super-critical state, and have reported various unique characteristics of the synthesized nanoparticles. Recently, it was also found that organic inorganic hybrid nanoparticles can be synthesized by the supercritical hydro-thermal synthesis. In this review, the specific features of hydrothermal synthesis are summarized.



**Figure 1** Kinetic of supercritical hydrothermal synthesis



**Figure 2** Apparatus for supercritical hydrothermal synthesis (ITEC Co., Ltd.)

## SUPERCritical WATER FOR HYDROTHERMAL SYNTHESIS

Supercritical water is in a state above the critical temperature (374°C) and pressure (22.1MPa) of water. Above the critical point, density of water varies greatly with a little change of temperature and pressure. Because of the drastic change of density, all the fluid properties change greatly around the critical point, including dielectric constant that is a controlling factor of reaction rate, equilibrium, and solubility of metal oxides. Dielectric constant of water at a room temperature is as high as 78, but it decreases gradually with temperature and, at around the critical point, drastically down to around 2 to 10, which is similar value to that of polar organic solvents (ethanol, acetone, etc.).

According to the variation of properties of water, phase behavior changes greatly around the critical point. Since supercritical water is of high-density steam, light gases like oxygen or hydrogen form a homogeneous phase with supercritical water. It should be noted that when the pressure is very high (namely the density of fluid is as high as of liquid), even if both water and organic compound are in supercritical state, phase separation occurs, just like liquid water-liquid oil phase separation.

Figure 1 shows how significant kinetics of hydro-thermal synthesis change around the critical point due to the variation of properties of water. The solubility also changes greatly around the critical point, first increases with increase of temperature and then decreases. This decrease of solubility is due to the lower density and dielectric constant. An estimation method of metal oxide solubility is described elsewhere. Figure 1 shows Arrhenius plot of the first-order reaction rate constant of hydrothermal synthesis, which was evaluated by using a flow-type apparatus. Arrhenius plot of kinetic constant shows a straight line below the critical point, but above the critical point increased two orders of magnitude. This is because of the decrease of dielectric constant; details of the mechanism was discussed elsewhere.

## SPECIFIC FEATURES OF SUPERCRITICAL HYDROTHERMAL SYNTHESIS

Figures 1 and 2 imply an essential point of our proposed method of nanoparticle synthesis at supercritical conditions: If metal salt solution is rapidly heated up to the critical state, fast hydrothermal synthesis occurs, where the formed metal oxide solubility is very low. Thus,

extremely high supersaturation degree of metal oxide is obtained to form nanoparticles. For achieving the fast heating of metal salt solution, a flow type apparatus shown in Figure 2 was employed (ITEC Co., Ltd.).

Metal salt solution was mixed with high-temperature water fed from another line to increase the temperature of the solution rapidly to the supercritical state and supercritical hydrothermal synthesis occurs just after the mixing point. The products were cooled and recovered as water-nanoparticles suspension through the back pressure regulator, with which pressure regulator, with which pressure of the system was controlled.

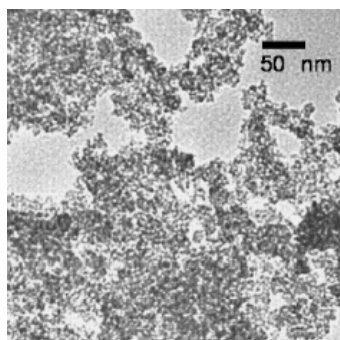
Figure 3 shows a TEM photo of  $\text{CoAl}_2\text{O}_4$  particles obtained by this method. As shown in this photo, the particle size is as small as 5 nm and the particle size distribution is very narrow, as shown in Figure 3.

Table 1 shows a list of the metal oxides synthesized by supercritical hydrothermal synthesis in our group. Basically, supercritical hydrothermal synthesis method is available for the metal oxides synthesized by conventional hydrothermal synthesis method. The different point is that nanometer size metal oxides could be synthesized, and crystallinity of the nanoparticles was much higher. In most cases, single crystals were formed. This sometimes leads to the specific characteristics of the products: Phosphor nanoparticles show high luminescence without heat treatment which is usually necessary for the products obtained by low-temperature wet method. Lithium ion battery cathode materials do not show the decay of the capacity even after the charge-discharge cycles, which has been considered as a major breakthrough point of materials. Kanamura et al. discussed about the mechanism and concluded that these particles are of single crystal, which is totally different from those obtained by the other methods.

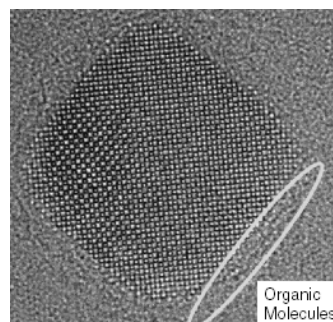
Ni nanoparticles could be obtained by this method. In this case,  $\text{HCOOH}$  was introduced as a reducing agent with nickel acetate solution. In supercritical water,  $\text{HCOOH}$  is decomposed into  $\text{H}_2$  and  $\text{CO}_2$ . An important point is that these gases and supercritical water form a homogeneous phase, and this mixture gas ( $\text{H}_2$  and  $\text{CO}_2$ ) shows higher reducing ability than  $\text{H}_2$  gas, as was reported in a literature. In a previous research of hydrogenation of hydrocarbons in

**Table 1** . Metal oxide nanoparticles synthesized by supercritical hydrothermal synthesis

Starting Materials	Products	Particle size (with organic modification)		References (with organic modification)
$\text{Al}(\text{NO}_3)_3$	$\text{AlOOH}$	20-1000	(5-20)	2,3,6,(20)
$\text{Ce}(\text{NO}_3)_3$	$\text{CeO}_2$	20-300	(2-10)	5, (22),
$\text{Co}(\text{NO}_3)_2$	$\text{Co}_3\text{O}_4$	$\approx 100$	(5-20)	2, (18)
$\text{Fe}(\text{NO}_3)_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\approx 50$	(5-20)	2, (18)
$\text{Fe}(\text{SO}_4)_3$	$\alpha\text{-Fe}_2\text{O}_3$	$\approx 50$		2
$\text{FeCl}_2$	$\alpha\text{-Fe}_2\text{O}_3$	$\approx 50$		2
$\text{Fe}(\text{NH}_4)_2\text{H}(\text{C}_6\text{H}_5\text{O}_7)_2$	$\text{Fe}_3\text{O}_4$	$\approx 50$		2
$\text{Gd}(\text{NO}_3)_2$	$\text{Gd}(\text{OH})_2$	$\approx 20$		2
$\text{Ni}(\text{NO}_3)_2$	$\text{NiO}$	$\approx 200$	(5-20)	12,15, (18)
$\text{Ni}(\text{CH}_3\text{COO})_2 + \text{H}_2$	$\text{Ni}$	$\approx 500$		15
$\text{Ni}(\text{phenanthroline}) + \text{H}_2$	$\text{Ni}$	$\approx 500$		12
$\text{Ti}(\text{SO}_4)_2$	$\text{TiO}_2$	$\approx 20$	(5-20)	2, (19)
$\text{TiCl}_4$	$\text{TiO}_2$	$\approx 20$		2
$\text{Zn}(\text{NO}_3)_2$	$\text{ZnO}$	$\approx 20$		16, 17, 25
$\text{ZrOCl}_2$	$\text{ZrO}_2$	$\approx 20$		2
$\text{Al}(\text{NO}_3)_3, \text{Co}(\text{NO}_3)_2$	$\text{CoAl}_2\text{O}_4$	5	(5)	24, (24)
$\text{Ba}(\text{NO}_3)_2, \text{Fe}(\text{NO}_3)_3,$	$\text{BaO}_6\text{Fe}_2\text{O}_3$	50-1000		4
$\text{Ba}(\text{NO}_3)_2, \text{Ti}(\text{SO}_4)_2$	$\text{BaTiO}_3$	50-1000		26
$\text{LiOH}, \text{Co}(\text{NO}_3)_2$	$\text{LiCoO}_2$	20-500		8,10, 23
$\text{LiOH}, \text{Mn}(\text{NO}_3)_2$	$\text{LiMn}_2\text{O}_4$	10-20		23
$\text{Al}(\text{NO}_3)_3, \text{Y}(\text{NO}_3)_3$	$\text{YAG Al}_3\text{Y}_3\text{O}_{12}$	20-600		7, 14
$\text{Al}(\text{NO}_3)_3, \text{Y}(\text{NO}_3)_3, \text{TbCl}_3$	$\text{Al}_5(\text{Y} + \text{Tb})_3\text{O}_{12}$	20-600		7, 14



**Figure 3** 5-nm  $\text{CoAl}_2\text{O}_4$  nanoparticles synthesized by supercritical hydrothermal synthesis.



**Figure 4** 7-nm size organic modified  $\text{CeO}_2$  nanocube synthesized at  $400^\circ\text{C}$  and 30 MPa.

supercritical water, it was elucidated that water-gas-shift reaction ( $\text{H}_2 + \text{CO}_2 = (\text{intermediates}) = \text{H}_2\text{O} + \text{CO}$ ) occurs rapidly under the condition and the intermediate specie formed during the reaction shows higher hydrogenating activity than  $\text{H}_2$  gas. This gives rise to the synthesis of uniform size Ni metal nanoparticles.

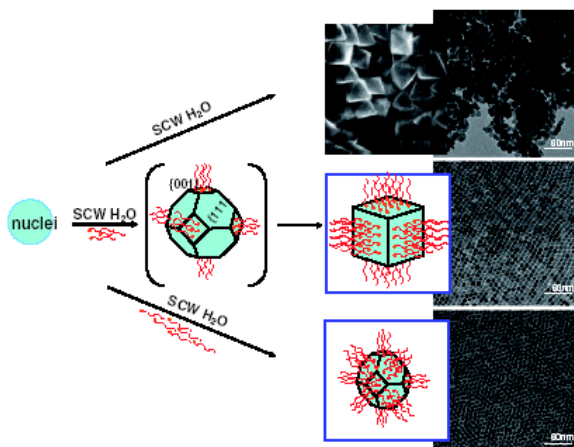
In a same manner, oxidizing reaction atmosphere is easily controlled by regulating oxygen gas partial pressure in the system.  $\text{LiMn}_2\text{O}_4$  nanocrystals, which is a Li ion battery cathode material, could be also synthesized by this method. For the synthesis of  $\text{LiMn}_2\text{O}_4$ ,  $\text{Mn}^{2+}$  of  $\text{Mn}(\text{NO}_3)_2$  should be oxidized to  $\text{Mn}^{3+}$ . For this purpose,  $\text{H}_2\text{O}_2$  was fed to the system.  $\text{H}_2\text{O}_2$  is decomposed at supercritical condition into oxygen gas, which forms a homogeneous phase with supercritical water to provide an excellent oxidizing atmosphere.

## ORGANIC INORGANIC HYBRID NANOPARTICLES

Hybrid materials of polymer-inorganic nanoparticle are considered to be promising new materials that show the trade-off functions between polymers and inorganics (light and high-mechanical strength, high thermal conductivity and electro-resistance, transparent flexible electro-conducting film, etc.) So far, tremendous efforts have been made to fabricate nanoparticle dispersed polymer, but it has been considered a difficult task to disperse the nanoparticles in organic solvents or in polymers, especially for the particles synthesized in hydrothermal conditions. This is because metal oxide particle surface is hydrophilic, and for the case of nanoparticles, it shows extremely high surface energy, which leads to the formation of aggregates.

Surface modification of nanoparticles with organic molecules is necessary for the dispersion of nanoparticles in solvents or in polymers. Silane-coupling agents are usually used for the organic modification of inorganic materials. However, for that purpose, at first nanoparticles should be dispersed in an organic solvent. Thus, organic modification by the coupling method is available only for the case of diluted phase so as the nanoparticles to be dispersed. By this method, a silica layer is formed on the surface of the nanoparticles, which sometimes changes the original properties of nanoparticles.

We proposed a new method to synthesize organic surface modified nanocrystals by introducing organic reagents during hydrothermal synthesis. Organic ligands and supercritical water forms a homogeneous phase and it is known that under the conditions water molecule itself



**Figure 5** Size and morphology change with the amount of organic ligands, and the hybrid nanoparticles form super lattice structures.



**Figure 6** Perfect dispersion of nanoparticles in organic solvents.

works as an acid or base catalyst for various organic reaction.

Figure 4 shows cerium oxide nanocube (7 nm) synthesized at 400 °C and 30 MPa. Decanoic acid was used as the organic ligands. From this TEM photo, it is known that organic ligands are bonded with surface Ce atoms.

With increasing the amounts of organic ligands, particles size was decreased and the morphology of the particles was changed from cubic to truncated octahedron. This is because the most reactive (001) surface is reacted with organic ligands, which suppresses the growth of this surface and forms the cubic shape nanoparticles. By introducing more amount of organic reagents, less reactive (111) surface is also modified with the organic ligands, which leads to the formation of polyhedron nanoparticles, as shown in Figure 5.

The surface modified nanoparticles synthesized by this method can be easily recovered by extraction with organic solvent from the water suspension phase, and well dispersed in organic solvents. Transparent solutions were obtained for the products, as shown in Figure 6. By using dynamic light scattering analysis, it was confirmed that particles are not aggregated, but suspended as an individual particles. By drying this solution, self-assembled super lattice structures were obtained, as shown in Figure 5 (right hand side TEM images). The gap between the particles on TEM image is around the double length of the organic modifier, which suggests the sufficient and uniform surface modification.

## REFERENCES :

- [1] T. ADSCHIRI, Chem. Lett., Vol. 36, **2007**, p. 1188
- [2] J. Zhang, S. Ohara, M. Umetsu, T. Naka, Y. Hatakeyama, T. Adschiri, Adv. Mater., 19, **2007**, p.203
- [3] K. Kaneko, K. Inoke, B. Freitag, Ana B. Hungria, Paul A. Midgley, Thomas W. Hansen, J. Zhang, S. Ohara, T. Adschiri, Nano Lett., 7, **2007**, p. 421
- [4] D. Rangappa, T. Naka, A. Kondo, M. Ishii, T. Kobayashi, T. Adschiri, J. Am. Chem. Soc., 129., **2007**, p. 11061
- [5] T. Mousavand1, S. Takami1, M. Umetsu1, S. Ohara, T. Adschiri, J. Mater. Sci., 41,**2006**, p.1445.