Highlight Review

Supercritical Hydrothermal Synthesis of Organic–Inorganic Hybrid Nanoparticles

Tadafumi Adschiri

(Received June 12, 2007; CL-078006)

Abstract

This paper summarizes specific features of supercritical hydrothermal synthesis: Namely, synthesis of nano single crystals and controllable oxidizing and reducing atmosphere. Synthesis of organic–inorganic hybrid nanoparticles is another unique feature of this method. The synthesized hybrid nanoparticles can be dispersed in organic solvents, from which super lattice structure can be formed.

◆ 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.

$$M(NO_3)_x + H_2O = M(OH)_x + xNHO_3$$

$$M(OH)_x = MO_{x/2} + \frac{x}{2}H_2O$$

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 Ostwalt ripening mechanism in high-temperature water.[1]

We proposed a method to synthesize nanometer size metal oxide rapidly and continuously at supercritical state, and have reported various unique characteristics of the synthesized nanoparticles.[2–18] Recently, it was also found that organic inorganic hybrid nanoparticles can be synthesized by the supercritical hydrothermal synthesis.[19–24] In this review, the specific features of hydrothermal synthesis are summarized.

◆ Supercritical Water for Hydrothermal Synthesis

Supercritical water is in a state above the critical temperature (374 °C) and pressure (22.1 MPa) 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. Figure 1 shows the critical loci for binary systems of organic

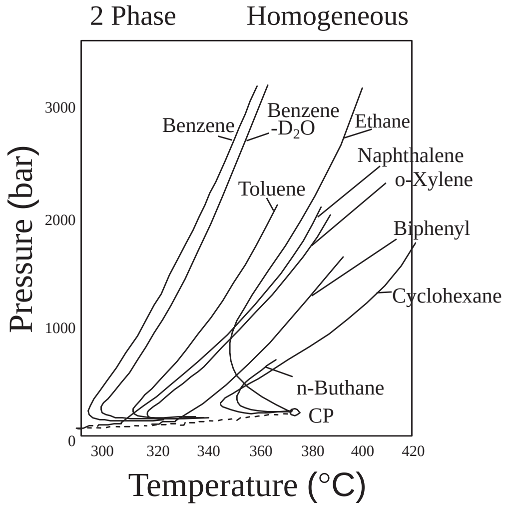

Figure 1. Phase behavior of binary systems for water–organic compounds.[25]

Prof. Tadafumi Adschiri,
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai 980-8577
E-mail: ajiri@tagen.tohoku.ac.jp

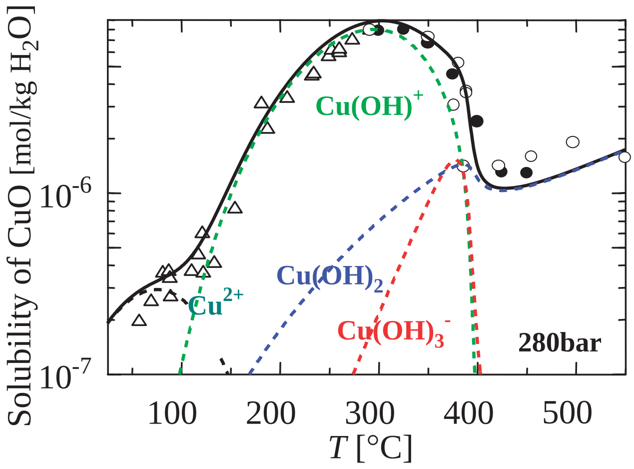

Figure 2. Solubility of CuO in high-temperature water.[26]

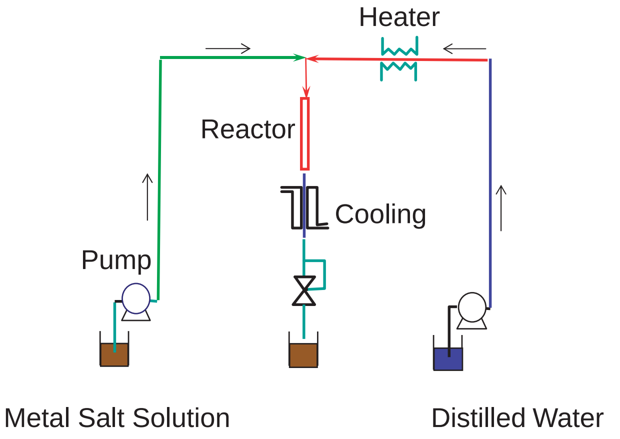

Figure 4. Apparatus for supercritical hydrothermal synthesis (ITEC Co., Ltd.).

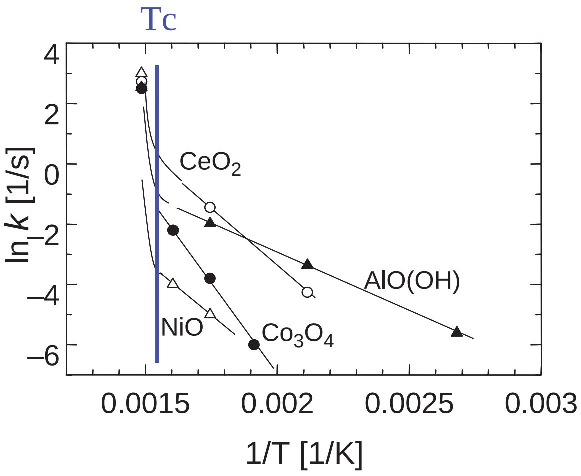

Figure 3. Kinetic of supercritical hydrothermal synthesis.[11]

compound and water.[25] The right-hand side of these curves, a homogeneous phase is formed at any composition. Organic compounds and water are not miscible at a low-temperature range, but forms a homogeneous phase at higher temperatures, which is because of the reduced dielectric constant of 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.

Figures 2 and 3 show how significant the solubility of metal oxides and kinetics of hydrothermal synthesis change around the critical point due to the variation of properties of water. Figure 2 shows the solubility of CuO in water over a wide range of temperature. The solubility 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.[26] Figure 3 shows Arrhenius plot of the first-order reaction rate constant of hydrothermal synthesis, which was evaluated by using a flow-type apparatus.[9,11] 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.[11]

◆ *Specific Features of Supercritical Hydrothermal Synthesis*

Figures 3 and 4 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 4 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 of the system was controlled.

Figure 5 shows a TEM photo of $CoAlO_3$ 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 5.[23]

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

Published on the web (Advance View) September 27, 2007; doi:10.1246/cl.2007.1188

Table 1. Metal oxide nanoparticles synthesized by supercritical hydrothermal synthesis

Starting Materials	Products	Particle size (with organic modification)		References (with organic modification)
$Al(NO_3)_3$	AlOOH	20–1000	(5–20)	2,3,6,(20)
$Ce(NO_3)_3$	CeO_2	20–300	(2–10)	5, (22),
$Co(NO_3)_2$	Co_3O_4	≈100	(5–20)	2, (18)
$Fe(NO_3)_3$	α-Fe_2O_3	≈50	(5–20)	2, (18)
$Fe(SO_4)_3$	α-Fe_2O_3	≈50		2
$FeCl_2$	α-Fe_2O_3	≈50		2
$Fe(NH_4)2H(C_6H_5O_7)_2$	Fe_3O_4	≈50		2
$Gd(NO_3)_2$	$Gd(OH)_2$	≈20		2
$Ni(NO_3)_2$	NiO	≈200	(5–20)	12,15, (18)
$Ni(CH_3COO)_2 + H_2$	Ni	≈500		15
Ni(phenanthororin) + H_2	Ni	≈500		12
$Ti(SO_4)_2$	TiO_2	≈20	(5–20)	2, (19)
$TiCl_4$	TiO_2	≈20		2
$Zn(NO_3)_2$	ZnO	≈20		16, 17, 25
$ZrOCl_2$	ZrO_2	≈20		2
$Al(NO_3)_3$, $Co(NO_3)_2$	$CoAl_2O_4$	5	(5)	24, (24)
$Ba(NO_3)_2$, $Fe(NO_3)_3$,	$BaO_6Fe_2O_3$	50–1000		4
$Ba(NO_3)_2$, $Ti(SO_4)_2$	$BaTiO_3$	50–1000		26
LiOH, $Co(NO_3)_2$	$LiCoO_2$	20–500		8,10, 23
LiOH, $Mn(NO_3)_2$	$LiMn_2O_4$	10–20		23
$Al(NO_3)_3$, $Y(NO_3)_3$	YAG $Al_5Y_3O_{12}$	20–600		7, 14
$Al(NO_3)_3$, $Y(NO_3)_3$, $TbCl_3$	$Al_5(Y + Tb)_3O_{12}$	20–600		7, 14

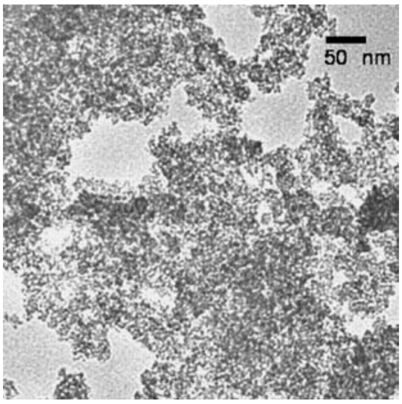

Figure 5. 5-nm $CoAl_2O_4$ nanoparticles synthesized by supercritical hydrothermal synthesis.[23]

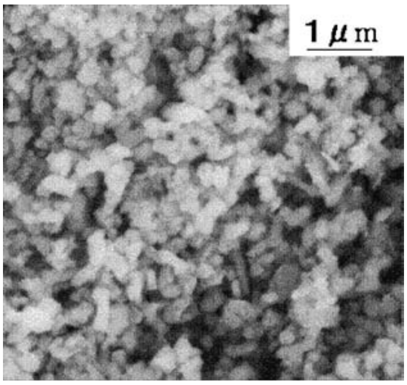

Figure 6. Ni nanoparticles formed from nickel acetate and Formic acid at 400 °C and 30 MPa.

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.[7,13] Lithium ion battery cathode materials (Figure 7) do not show the decay of the capacity even after the charge–discharge cycles,[8,10] which has been considered as a major breakthough point of the 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.[16]

Figure 6 shows Ni nanoparticles obtained by this method. In this case, HCOOH was introduced as a reducing agent with nickel acetate solution.[12,14] In supercritical water, HCOOH is decomposed into H_2 and CO_2. An important point is that these gases and supercritical water form a homogeneous phase, and this mixture gas (H_2 and CO_2) shows higher reducing ability than H_2 gas, as was reported in a literature.[27,28] In a previous re-

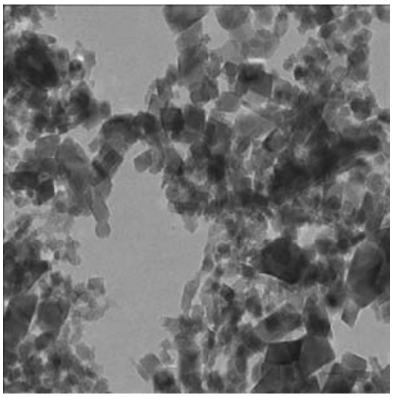

Figure 7. $LiMn_2O_4$ nanoparticles (10–20 nm) synthesized from LiOH, $Mn(NO_3)_2$, and H_2O_2, at 400 °C and 30 MPa.

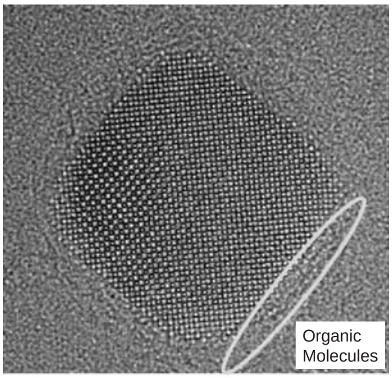

Figure 8. 7-nm size organic modified CeO_2 nanocube synthesized at 400 °C and 30 MPa.[22,23]

search of hydrogenation of hydrocarbons in supercritical water, it was elucidated that water-gas-shift reaction ($H_2 + CO_2 =$ (intermediates) $= H_2O + CO$) occurs rapidly under the condition and the intermediate species formed during the reaction shows higher hydrogenating activity than H_2 gas.[27,28] This gives rise to the synthesis of uniform size Ni metal nanoparticles, as shown in Figure 6.

In a same manner, oxidizing reaction atmosphere is easily controlled by regulating oxygen gas partial pressure in the system. Figure 7 shows $LiMn_2O_4$ nanocrystals, which is a Li ion battery cathode material. For the syhnthesis of $LiMn_2O_4$, Mn^{2+} of $Mn(NO_3)_2$ should be oxidized to Mn^{3+}. For this purpose, H_2O_2 was fed to the system. H_2O_2 is decomposed at supercritical condition into oxygen gas, which forms a homogeneous phase with supercritical water to provide an excellent oxidizing atmosphere.[8,10,16]

♦ 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 works as an acid or base catalyst for various organic reaction.[19–24]

Figure 8 shows cerium oxide nanocube (7 nm) synthesized at 400 °C and 30 MPa.[22] Decanoic acid was used as the organic ligands. From this TEM photo, it is known that organic ligands are bonded with surface Ce atoms.[23]

With increasing the amounts of organic ligands, particles size was decreased and the morphology of the particles was changed from cubic to truncated octahedron.[22] 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,[22] as shown in Figure 9.

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 10. 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 9 (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.[19–24]

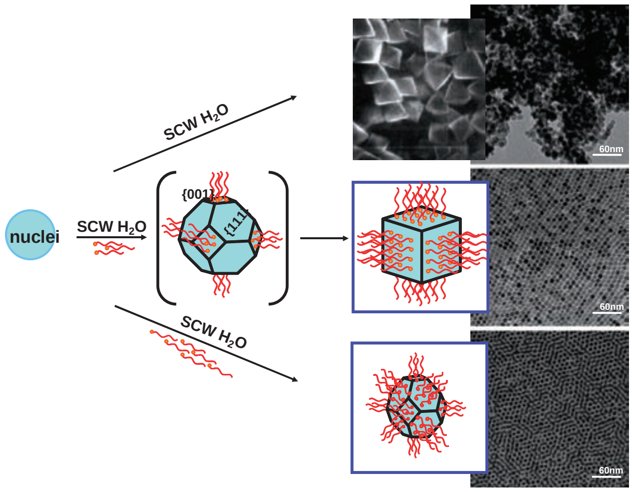

Figure 9. Size and morphology change with the amount of organic ligands, and the hybrid nanoparticles form super latticle structures.[22]

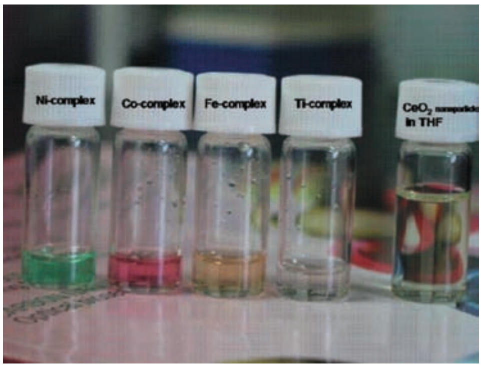

Figure 10. Perfect dispersion of nanoparticles in organic solvents.

Conclusion

Supercritical hydrothermal synthesis with flow-type apparatus provides metal oxide nanoparticles with narrow particle size distribution (5 to several 10 nm). Since the temperature is higher than the conventional hydrothermal synthesis method, higher crystallinity is obtained: In most cases, single crystals are formed. Since supercritical water is miscible with oxygen or hydrogen gas, oxidizing or reducing atmosphere can be easily controlled by regulating oxygen or hydrogen partial pressure in the systems. At supercritical state a homogeneous phase is formed for water and organic molecules, and water molecule itself acts as acid or base catalysts for organic reactions. This is the reason why organic surface modified metal oxide nanoparticles (2 to 10 nm) could be synthesized by supercritical hydrothermal synthesis. The organic–inorganic hybrid nanoparticles could be well dispersed in organic solvents and forms a self-assembled super lattice structure. Because of its unique characteristics, the hybrid nanoparticles are expected to be used for many applications including polymer–inorganic hybrid materials, medical imaging and therapy, semiconductor materials, etc.

References and Notes

1 K. Byrappa, M. Yoshimura, in *Handbook of Hydrothermal Technology*, Noyes Publications, NewJersey, USA, **2001**.
2 T. Adschiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc.* **1992**, *75*, 1019.
3 T. Adschiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc.* **1992**, *75*, 2615.
4 Y. Hakuta, T. Adschiri, T. Suzuki, T. Chida, K. Seino, K. Arai, *J. Am. Ceram. Soc.* **1998**, *81*, 2461.
5 Y. Hakuta, S. Onai, H. Terayama, T. Adschiri, K. Arai, *J. Mater. Sci. Lett.* **1998**, *17*, 1211.
6 Y. Hakuta, T. Adschiri, H. Hirakoso, K. Arai, *Fluid Phase Equilib.* **1999**, *158–160*, 733.
7 Y. Hakuta, K. Seino, H. Ura, T. Adschiri, H. Takizawa, K. Arai, *J. Mater. Chem.* **1999**, *9*, 2671.
8 K. Kanamura, A. Goto, R. Y. Ho, T. Umegaki, K. Toyoshima, K. Okada, Y. Hakuta, T. Adschiri, K. Arai, *Electrochem. Solid-State Lett.* **2000**, *3*, 256.
9 T. Adschiri, Y. Hakuta, K. Arai, *Ind. Eng. Chem. Res.* **2000**, *39*, 4901.
10 T. Adschirib, Y. Hakuta, K. Kanamura, K. Arai, *High Pressure Res.* **2001**, *20*, 373.
11 T. Adschiri, Y. Hakuta, K. Sue, K. Arai, *J. Nanopart. Res.* **2001**, *3*, 227.
12 M. le Clercq, T. Adschiri, K. Arai, *Biomass Energy* **2001**, *21*, 73.
13 Y. Hakuta, T. Haganuma, K. Sue, T. Adschiri, K. Arai, *Mater. Res. Bull.* **2003**, *38*, 1257.
14 K. Sue, N. Kakinuma, T. Adschiri, K. Arai, *Ind. Eng. Chem. Res.* **2004**, *43*, 2073.
15 S. Ohara, T. Mousavand, M. Umetsu, S. Takami, T. Adschiri, Y. Kuroki, M. Takata, *Solid State Ionics* **2004**, *172*, 261.
16 K. Kanamura, T. Umegaki, K. Toyoshima, KI Okada, Y. Hakuta, T. Adschiri, K. Arai, "Key Engineering Materials (Electroceramics in JAPAN III)," Vol. 181-1, pp. 147–150.
17 M. Atashfaraz, M. Shariaty-Niassar, S. Ohara, M. Umetsu, T. Naka, T. Adschiri, *Fluid Phase Equilib.* **2007**, 257, 2, pp. 233–237.
18 S. Ohara, T. Mousavand, T. Sasaki, M. Umetsu, T. Naka, T. Adschiri, *J. Mater. Sci.* **2007**, in press.
19 T. Mousavand, S. Takami, M. Umetsu, S. Ohara, T. Adschiri, *J. Mater. Sci.* **2006**, *41*, 1445.
20 T. Mousavand, J. Zhang, S. Ohara, M. Umetsu, T. Naka, T. Adschiri, *J. Nanopart. Res.* **2007**, *6*, 9186.
21 T. Mousavand, S. Ohara, M. Umetsu, J. Zhang, S. Takami, T. Naka, T. Adschiri, *J. Supercrit. Fluids* **2007**, *40*, 397.
22 J. Zhang, S. Ohara, M. Umetsu, T. Naka, Y. Hatakeyama, T. Adschiri, *Adv. Mater.* **2007**, *19*, 203.

23 K. Kaneko, K. Inoke, B. Freitag, A. B. Hungria, P. A. Midgley, T. W. Hansen, J. Zhang, S. Ohara, T. Adschiri, *Nano Lett.* **2007**, *7*, 421.

24 D. Rangappa, T. Naka, A. Kondo, M. Ishii, T. Kobayashi, T. Adschiri, *J. Am. Chem. Soc.* **2007**, in press.

25 E. U. Franck, *Pure Appl. Chem.* **1981**, *53*, 1401.

26 K. Sue, T. Adschiri, K. Arai, *Ind. Eng. Chem. Res.* **2002**, *41*, 3298.

27 T. Adschiri, R. Shibata, T. Sato, M. Watanabe, K. Arai, *Ind. Eng. Chem. Res.* **1998**, *37*, 2634.

28 T. Adschiri, S. Okazaki, M. Mochiduki, S. Kurosawa, K. Arai, *Int. J. Soc. Mater. Eng. Resources* **1999**, *7*, 273.