

Synthesis of nano sized particles using supercritical fluids

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INTRODUCTION

Nanoparticles of metal and metal oxides are important materials due to its various applications such as electrical industries, biomedical area, catalyst industries, material industries, and so on. To synthesize metal and metal oxide, various methods have been developed such as a chemical reduction, sol-gel process, co-precipitation method, hydrothermal process, solvothermal process and so on. [1-6] However, these methods require a long reaction time to obtain final products. For the synthesis of metal oxide, the calcination process to obtain highly crystalline products causes the aggregation of the particles.

In recent years, the syntheses of metal and metal oxide particles in supercritical fluids have been extensively reported. [7-9] Especially, supercritical water and alcohol are promising reaction media for producing the inorganic nanoparticles with controlling size, morphology and crystalline structure of the particles. Supercritical fluids have the low dielectric constant with respect to high temperature and pressure induces the fast nucleation, and thus small particles can be achieved. Moreover, it is possible to prepare inorganic materials having high crystallinity without calcination which lead, and thus the aggregation of the nanoparticles can be avoided.

In this study, Ni, CeO₂, ZnO and BaTiO₃ nanoparticles were synthesized by the hydrothermal/solvothermal methods in supercritical water and methanol. It was confirmed that the formations of inorganic nanoparticles achieved in just a few minutes of reaction without aging or calcination. To determine the reaction mechanism, the effects of variables such as temperature, reaction time and concentration were investigated.

MATERIALS AND METHODS

Ni, CeO₂, ZnO and BaTiO₃ nanoparticles were synthesized using supercritical water and methanol. Methanol (or water) containing starting materials for synthesizing metal and metal oxide nanoparticles were introduced into a batch reactor (SUS 316, 23 ml). After sealing, the reactor was immersed into the molten salt bath which was heated to a desired temperature, and constantly shaken for a certain time. After the reaction, the reactor was cooled rapidly to a room temperature by immersing in cold water. The resulting powders were isolated by a centrifugation, and washed with water and methanol several times. Then, the products were dried in a vacuum oven overnight at 40 °C. Experimental details for synthesizing metal and metal oxide nanoparticles are listed in Table 1. Ni(OH)₂·6H₂O, Ce(OH)₄ and Zn(OH)₂ were

prepared by adding NaOH to the solution dissolving Ni(NO₃)₂, Ce(NO₃)₄·6H₂O and Zn(NO₃)₂·6H₂O.

Table 1. Composition and experimental conditions for Co, Ni, CeO₂, ZnO and BaTiO₃.

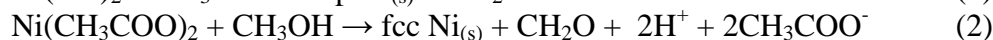
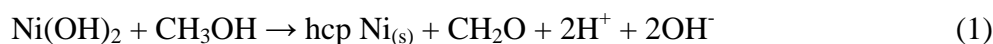
Target material	Starting material	Reaction medium	Temp. (°C)	Pressure (bar)	Time (min)	Surface modifier
Ni	Ni(OH) ₂ , Ni(CH ₃ COO) ₂	methanol	300, 400	300	10	-
CeO ₂	Ce(OH) ₄	methanol, water	350 ~ 400	250 ~ 300	10	decanoic acid, oleic acid
ZnO	Zn(OH) ₂	methanol	300	250	10	CTAB
BaTiO ₃	Ba(OH) ₂ + TiO ₂ (anatase)	water	400	300	5 ~ 30	-

The particles synthesized were characterized by HR-TEM (high resolution transmission electron microscope), FE-SEM (field emission scanning electron microscope), and XRD (X-ray diffraction).

RESULTS

1. Nickel

Fig. 1 shows XRD patterns of Ni particles synthesized in supercritical methanol. When Ni(OH)₂ was used as a starting material, the mixture of hcp and fcc Ni was obtained at 300 °C and 300 bar, and the higher temperature (400 °C) led to the formation of pure hcp Ni (JCPDS Card No. 45-1027) as shown in Fig. 1a and b. On the contrary, the use of Ni(CH₃COO)₂ as a starting material yielded pure fcc Ni (JCPDS Card No. 04-0850). It is well-known that the methanol acts not only as the reaction medium but also reducing agent. The proposed mechanisms of the formation of Ni from Ni(CH₃COO)₂ are as follows.



By comparing fig. 1a to fig. 1c, it can be concluded that solvothermal method using supercritical methanol provides phase controllable synthesis of Ni nanoparticles.

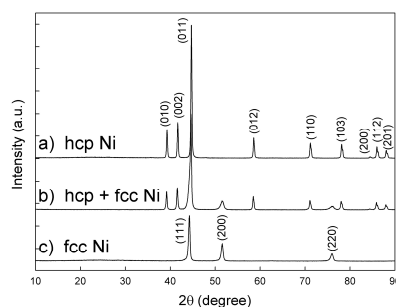


Figure 1. X-ray diffraction patterns of Ni synthesized from (a) Ni(OH)₂ at 400 °C and 300 bar, (b) Ni(OH)₂ at 300 °C and 300 bar, and (c) Ni(CH₃COO)₂ at 400 °C and 300 bar.

2. Ceria (CeO_2)

Fig. 2 shows TEM images of synthesized CeO_2 nanoparticles under supercritical water and methanol. In both cases, ceria nanoparticles (~ 20 nm) were successfully obtained without any stabilizer, and ceria particles synthesized in supercritical methanol is smaller than those synthesized in supercritical water. This result can be explained by the density and dielectric constant of the solvent. Supersaturation of solute occurs more quickly when the density and dielectric constant of solvent are lower, which makes the nuclei smaller. Methanol shows lower density and dielectric constant than water at the same condition, and thus lead to the fast nucleation, which can achieve the formation of smaller particles.

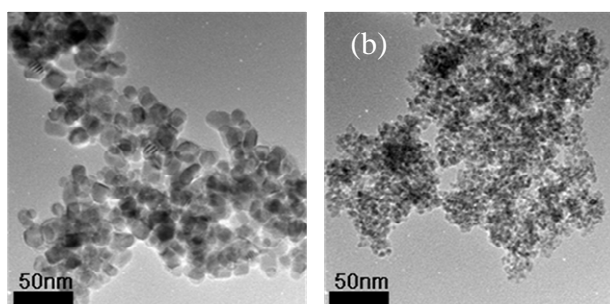


Figure 2. TEM images of ceria particles synthesized in (a) supercritical water and (b) supercritical methanol without surface modifier at 400 °C and 300 bar.

When the experiments were performed in the presence of the surface modifiers, the smaller and well-dispersed ceria nanoparticles (~ 10 nm) could be obtained than those synthesized without a surface modifier as shown in Fig. 3. With decanoic acid, the ceria particles showed pebble-like shape, and the average particle size was 5.5 nm. When oleic acid was used, ceria particles with a cubic shape were observed, and the average size was 8 nm.

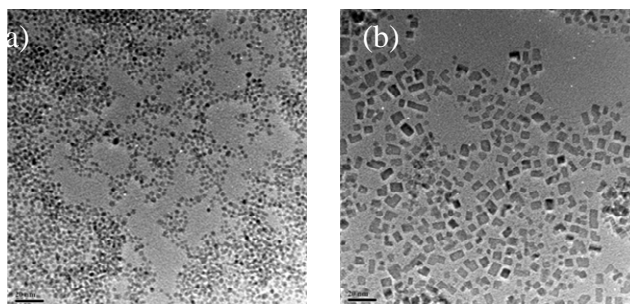


Figure 3. TEM images of ceria nanoparticles synthesized in supercritical methanol at 350 °C and 250 bar in the presence of (a) decanoic acid and (b) oleic acid as surface modifiers.

3. Zinc oxide (ZnO)

CTAB (cetyltrimethylamine bromide) has been widely used as a surfactant to induce the 1-dimensional growth of metal/metal oxide particles. [10, 11] Fig. 4 shows the effect of CTAB on the morphology of the ZnO particles. Without CTAB, ZnO particles with the irregular shapes were obtained. When the initial $[\text{CTAB}] : [\text{Zn}(\text{OH})_2]$ molar ratio was 0.2, the rod-shaped ZnO particles were formed (width : 20 nm, length : 100 ~ 200 nm). However, for the

high CTAB concentration, spherical particles (15 ~ 40 nm) were observed as shown in Fig. 4c. It is suggested that, at high CTAB concentration, CTAB molecules were adsorbed on the entire crystal faces, and thus the 1-dimensional growth did not occur.

The fact that initial molar ratio of Zn precursors and CTAB can control morphology of zinc oxide particles was also confirmed by comparing XRD patterns. XRD patterns of synthesized zinc oxide particles were shown in Fig. 5. The XRD pattern of rod-type ZnO particles shows that the intensity at $2\theta = 34.4^\circ$ indicating (002) planes is higher than that attributed to (100) planes ($2\theta = 31.6^\circ$), while the XRD pattern of spherical ZnO shows low peak intensity of (002) planes. From this result, it is suggested that the use of CTAB leads to the predominant growth of (002) planes, and then the ZnO particles with 1-D structure can be obtained.

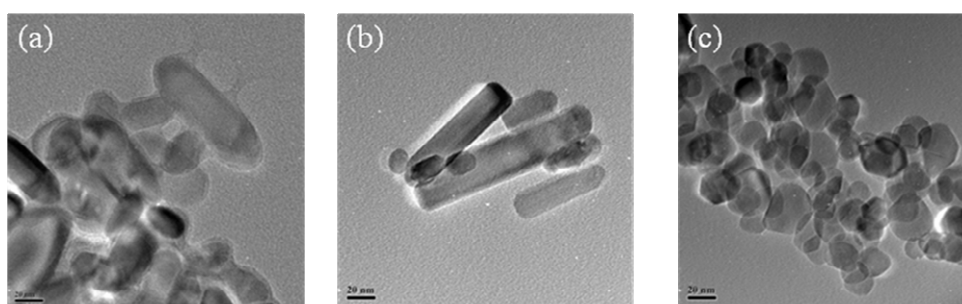


Figure 4. HR-TEM images of ZnO particles synthesized in supercritical methanol at 300 °C and 250 bar (a) without a surfactant, and with CTAB at the initial [CTAB] : [Zn(OH)₂] molar ratio of (b) 0.2 and (c) 1.

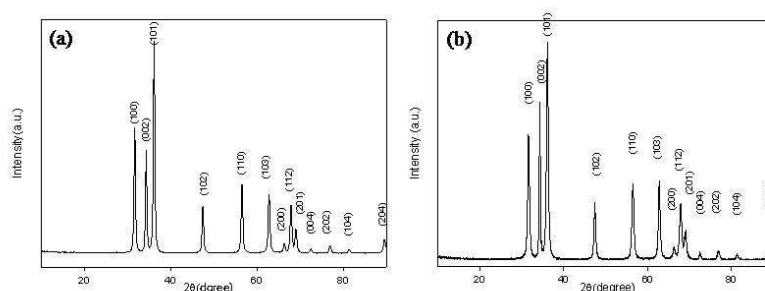
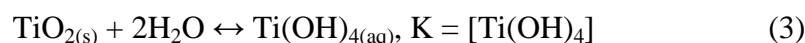


Figure 5. XRD patterns of ZnO particles synthesized in supercritical methanol at 300 °C and 250 bar with CTAB at the initial [CTAB] : [Zn(OH)₂] molar ratio of (a) 1 and (b) 0.2.

4. Barium titanate (BaTiO₃)

Fig. 6 shows the effects of the initial molar ratio of Ba(OH)₂ to TiO₂ (anatase), reaction time and KOH. As the initial Ba(OH)₂ concentration and reaction time increased, the content of TiO₂ (anatase) in the product was reduced, but the small amount of anatase still remained. When KOH was used as a [OH⁻] source, the main peak indicating anatase disappeared. In supercritical water, anatase is reacted with water as follows. [12]



In this reaction, an increase in [OH⁻] concentration induces a forward reaction. Thus, KOH increased solubility of anatase in supercritical water. Adding KOH is effective for make solubility of anatase in supercritical water due to its strong basity.

Fig. 7 shows TEM images of BaTiO₃ nanoparticles synthesized in supercritical water. BaTiO₃ nanoparticles (~ 100 nm) with a cubic shape were successfully obtained without any stabilizer.

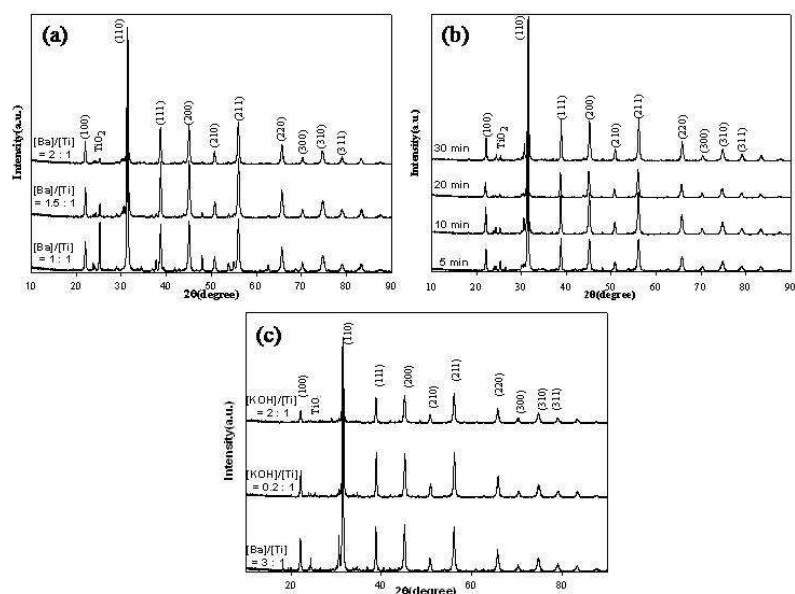


Figure 6. XRD patterns of BaTiO₃ particles synthesized in supercritical water at 400 °C and 300 bar; the effects of (a) the initial [Ba] : [Ti] molar ratio (for 20 min), (b) reaction time and (c) KOH (for 10 min).

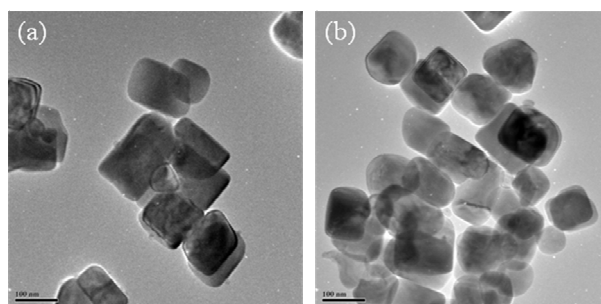


Figure 7. HR-TEM images of BaTiO₃ nanoparticles synthesized in supercritical water at 400 °C and 300 bar for the initial [Ba] : [Ti] molar ratio of 2; (a) reaction time is 20 min, and (b) reaction time is 10 min in the presence of additional KOH ([KOH] : [TiO₂] = 0.5 : 1).

CONCLUSION

In summary, supercritical methanol acts not only as the reaction medium but also the reducing agent, in synthesis of pure metal particles. Thus, Ni particles were synthesized without addition of reducing agent. In addition, phase-controlled synthesis of Ni particles was achieved by changing starting materials.

For metal oxides such as CeO₂ and ZnO, morphology and size of particles were controlled by surface modifiers such as decanoic acid, oleic acid and CTAB. Barium titanate, one of important ferroelectric nanoparticles was synthesized in supercritical water, and it was observed that reaction time and molar ratio of barium hydroxide to anatase affect conversion of anatase. Adding KOH achieved the BaTiO₃ nanoparticles with the high purity.

Hydrothermal/solvothermal method using supercritical fluid provides effective process to synthesize metal/metal oxide nanoparticles. As mentioned previously, process using supercritical fluid need short reaction time and can eco-friendly process.

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