

Ex-situ Surface Modification of BaTiO₃ Nanoparticles Prepared by Hydrothermal Synthesis

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Abstract—Controlling the surface of nanoparticles is increasingly becoming important to develop next generation of nanoparticles. In this work, surface modification of BaTiO₃ nanoparticles after hydrothermal synthesis was examined by adding modifier reagent to the hydrothermally synthesized BaTiO₃ nanoparticles. The results showed that reagent successfully modified and controlled the surface of the BaTiO₃ nanoparticles.

Index Terms—BaTiO₃, Ex-situ surface modification, nanoparticles.

I. INTRODUCTION

BaTiO₃ is widely used in electro-ceramics industries. For example, in IT industry, packaging of semiconductor devices is an important issue for eliminating the noise from outside the package of the IT tips. One method for solving this problem is to elevate the dielectric constant of the packaging plastics.

To elevate the dielectric constant of plastics, mixing with high dielectric constant materials such as BaTiO₃ is effective. For that purpose, it is also required to produce BaTiO₃ particles with small particle size (<100 nm), narrow particle size distribution and hydrophobic surface property.

There are many methods for synthesizing fine BaTiO₃ powder such as coprecipitation [1], sol-gel method [2]-[7] and hydrothermal method [8]-[24], etc. However, the BaTiO₃ particles produced by these methods aren't smaller than 100 nm in diameter and particle size distribution isn't sufficiently narrow for the packaging nano hybrid materials.

In this study, we examined the surface modification of BaTiO₃ nanoparticles (<100 nm) after their hydrothermal synthesis using phenol as modifier.

Manuscript received February 12, 2008. This work was supported by a scientific research grant from the Ministry of Education, Science, Sports, and Culture of Japan. This research was also supported by a Grant-in-Aid for COE project, Giant Molecules and Complex Systems.

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II. EXPERIMENTAL METHOD

At first, batch type hydrothermal synthesis of BaTiO₃ nanoparticles was performed using a pressure resistant tube reactor (SUS 316) with the inner volume of 5.0 mL. The reactor was loaded with 0.01 mol/L barium hydroxide octahydrate (Wako Pure Chemical Industrials) and titanium dioxide (30wt%, Ishihara sangyo kaisha) water suspension. Thereafter, the reactor was tightly capped and put in an electric furnace. Heating rate up to the temperature was about 3 min. Experiments were performed at 400 °C and 30 MPa for 10 min and terminated by quenching the reactor in a water bath at room temperature. After recovering the products, they were rinsed by distilled water. Then, the products were dried at 60 °C during over night.

Next, for Ex-situ surface modification of synthesized BaTiO₃ nanoparticles, the reactor was loaded with 0.01 mol/L BaTiO₃ aqueous solution. To modify the surfaces of the nanoparticles, 0.1 mL of phenol was also added to the reactor. Finally, the reactor was tightly capped and put in the electric furnace whose temperature was maintained at 200 °C with 40 MPa pressure. The reaction was performed for 15 min and terminated by quenching the reactor in the water bath at room temperature again. After recovering the products, they were purified by tetrahydrofuran and distilled water and the products were dried under vacuum over night.

III. CHARACTERIZATION

To identify the property of the purified products, all products were characterized as follows. The crystallographic identity of the synthesized nanoparticles was investigated by an X-ray diffraction (XRD) measurement. XRD data was recovered at room temperature on a Dmax γ_n X-ray diffractometer (Rigaku) with CuK α radiation. The presence of the chemical bonds on the surfaces of the nanoparticles was evaluated by a Fourier transform infrared spectroscopy (FTIR, FT/IR-680 plus-JASCO) with an attenuated total reflection (ATR PRO400-S) attachment. The size and shape of the nanoparticles were studied by using a transmission electron microscopy (TEM, JEM-1200 EX II (JEOL, Ltd.)).

IV. RESULTS AND DISCUSSION

TEM images of the synthesized nanoparticles are shown in fig. 1.

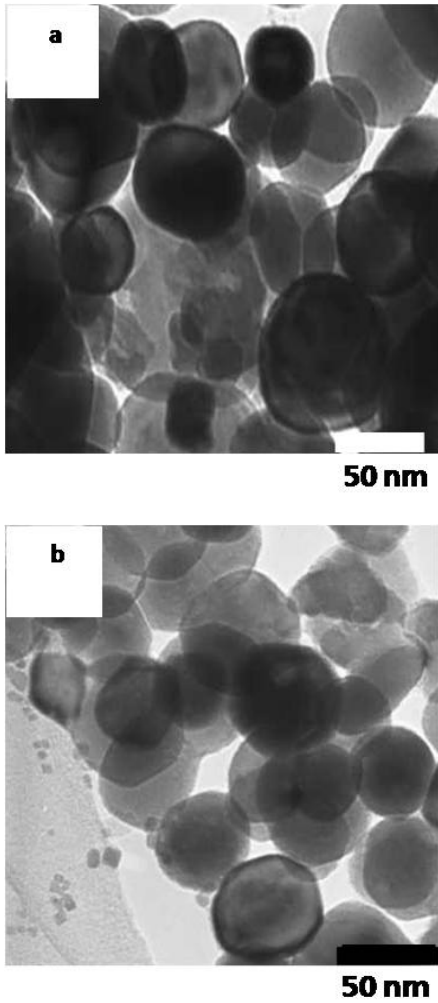


Fig. 1- TEM images of the (a) synthesized BaTiO₃ nanoparticles at 400 °C, 30 MPa and (b) BaTiO₃ nanoparticles modified with phenol at 200 °C, 40 MPa.

Fig. 1a shows BaTiO₃ nanoparticles synthesized without reagent at 400°C, 30MPa and fig. 1b shows ex-situ surface modified BaTiO₃ nanoparticles with phenol at 200 °C, 40 MPa. In both condition particle size and also shape are almost same.

The results of XRD analysis in fig. 2 show that in both condition single phase BaTiO₃ nanoparticles have been obtained. The vertical lines in fig. 2 indicate the peak positions of standard tetragonal phase BaTiO₃ according to JCPDS No. 05-0626. The XRD patterns of modified and unmodified particles are the same. This suggests that tetragonality of BaTiO₃ does not change with ex-situ surface modification.

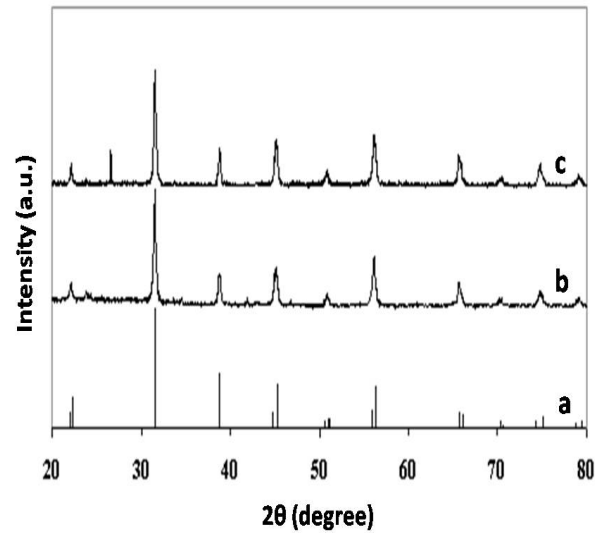


Fig. 2- XRD patterns of (a) standard tetragonal BaTiO₃, (b) Synthesized BaTiO₃ nanoparticles without reagent at 400 °C, 30 MPa and (c) Ex-situ modified BaTiO₃ nanoparticles with phenol at 200 °C, 40 MPa.

To determine the surface properties of the BaTiO₃ nanoparticles, we examined their dispersibility in a binary system of toluene and water. Fig. 3 demonstrates that the ex-situ modified nanoparticles were dispersed in the organic phase (fig. 3) instead of water phase.

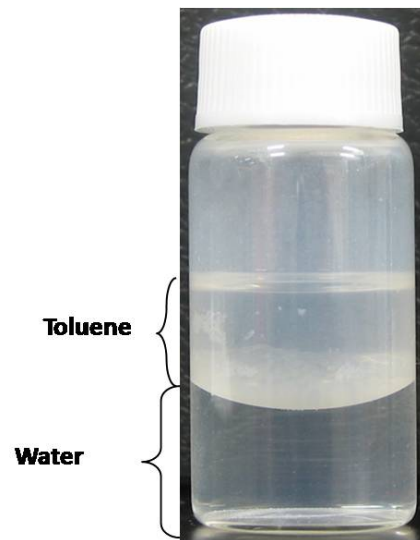


Fig. 3-Dispersibility of the Ex-situ surface modified BaTiO₃ nanoparticles with phenol at 200 °C, 40 MPa.

This result indicates that the surface property of the BaTiO₃ nanoparticles was changed from hydrophilic to hydrophobic by the addition of modifier reagent.

In order to investigate the chemical bonding on the surface of nanoparticles, fig. 4 shows the FTIR spectra of the unmodified and also modified BaTiO₃ with phenol. On the modified spectra, appearance the new absorption peaks around 1600 and 3600 cm⁻¹ correspond to ring and OH bonds on the surface of the ex-situ modified particles.

Then, it can be concluded that the nanoparticles modified with reagent have chemically organic coverage on their surface.

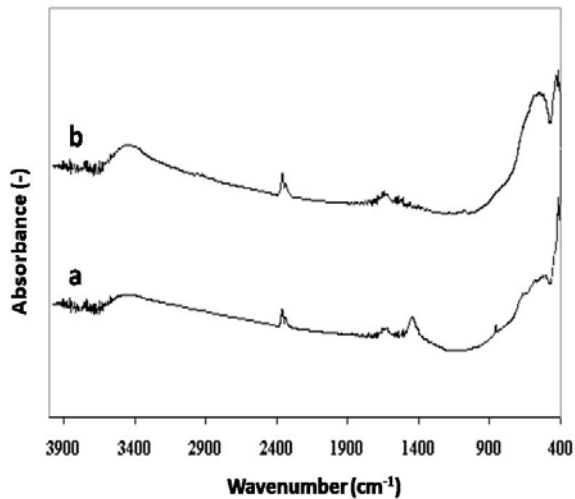


Fig. 4- FTIR spectra of BaTiO₃ nanoparticles (a) synthesized without reagent at 400 °C, 30 MPa and (b) Ex-situ modified BaTiO₃ nanoparticles with phenol at 200 °C, 40 MPa.

V. CONCLUSION

BaTiO₃ is used in various applications that the control of its surface affects on performance. In this study, ex-situ surface modification of hydrothermally synthesized BaTiO₃ nanoparticles was performed. The results showed that the phenol could change the surface property of BaTiO₃ nanoparticles.

ACKNOWLEDGMENT

This work was supported by a Scientific Research Grant from the ministry of Education, Science, Sports, and culture of Japan (T.A). This research was also partly supported by a Grant-in-Aid for the COE project, Giant Molecules and Complex Systems.

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