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FERROELECTRICS

Preparation of barium titanate nanocube particles by solvothermal method and their characterization

Satoshi Wada · A. Nozawa · M. Ohno · H. Kakemoto · T. Tsurumi · Y. Kameshima · Y. Ohba

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Abstract Barium titanate ($BaTiO_3$) nanocube particles below 20 nm were prepared by solvothermal method. A selection of organic solvent and inorganic materials of Ba and Ti sources was most important for the preparation of nanocubes. A nucleation and particle growth of $BaTiO_3$ nanoparticles led to a formation of the $BaTiO_3$ nanocubes with a size of 10–15 nm at temperatures above 200 °C.

Introduction

Traditional ceramics processing was composed of three main processes, i.e., (1) preparation of ceramics powders, (2) preparation of compact by pressing of the powders, and (3) sintering of the compact at high temperature (usually about 70% of the melting point). In this process, the most important step was the sintering procedure, and the preparation of powders has not been focused on so much. Recent use of nano-sized powders has led to attempts to reduce the sintering temperature [1–3]. However, a basic idea of the preparation of ceramics did not change from B.C. 10000 to present day. We should now consider the future ceramics processing on the basis of the future devices. A nano-controlled structure will be a key issue to enhance or create new properties of the future devices and materials. The high temperature sintering process cannot be used then. The nano-sized structures cannot persist at high temperature because of fast diffusion. What is the future ceramics processing? We believe there should be no sintering process to induce nano-ordered structures. The absence of sintering means there is no diffusion process, which suggests that different nanoparticles could be self-arranged or self-organized. Moreover, we must control the size and the shape of ceramic nanoparticles if dense ceramics is required. In respect of the future ceramics processing, the nanocubes with a narrow size distribution should be prepared as minimum-sized parts at first. Then, the mm-sized materials should be built up using the nanocubes. The factors positively affecting the bonding between the nanocubes should be thought over as well. A room temperature junction of the nanocubes is one of them. This phenomenon has been well-known as a room temperature sintering between silver nanoparticles with active and fresh surfaces. The most cases of the room temperature junction were reported for metal materials. However, there were a few reports [4, 5] about the room temperature junction of oxide materials. Therefore, we believe that the most important key point for the future ceramics processing is the preparation of the nanocube particles with a narrow size distribution and a normalized size despite chemical composition.

In this study, we have tried to prepare the nanocube particles with sizes of around 10 nm. For this purpose, barium titanate ($BaTiO_3$) was selected. This is because $BaTiO_3$ is a complex oxide material, and as compared to titanium dioxide or zinc oxide, it is very difficult to prepare shape-controlled nanoparticles. The $BaTiO_3$ particles have been used as raw materials for a dielectric device application such as multi layered ceramics capacitor (MLCC).

S. Wada (✉) · A. Nozawa
Material Science and Technology, Interdisciplinary Graduate School of Medical and Engineering, University of Yamanashi, 4-4-37 Takeda, Kofu, Yamanashi 400-8510, Japan
e-mail: swada@yamanashi.ac.jp

M. Ohno · H. Kakemoto · T. Tsurumi · Y. Kameshima · Y. Ohba
Department of Metallurgy and Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8552, Japan

Many researchers have tried to prepare size and shape controlled $BaTiO_3$ nanoparticles. To date, the preparation of the $BaTiO_3$ nanocube particles was reported by a couple of researchers. Hou et al. [6] and Yan et al. [7] reported the preparation of $BaTiO_3$ nanocube particles, but their particle sizes were from 40 to 90 nm with round-corner. So far, there are no $BaTiO_3$ nanocube particles with sizes of around 10 nm with sharp-edge corner worldwide. In this study, our target is to prepare the $BaTiO_3$ nanocube particles with sharp-edge and sizes at around 10 nm.

Experimental

The $BaTiO_3$ nanocube particles were prepared by a solvothermal method [6, 7]. There are a lot of parameters such as solvent, raw materials for $BaTiO_3$, temperature, soaking time, concentration, and pressure in this method. These parameters were investigated precisely. In this study, among these parameters, kinds of solvents were mostly focused to prepare nanocubes as the most important parameter, and then, the size and shape dependences of $BaTiO_3$ nanoparticles on solvent and raw materials for $BaTiO_3$ are investigated here. While water, ethanol and 2-methoxyethanol were used as the solvents while titanium dioxide (TiO_2, retile structure, size: 7 nm, Ishihara Co., Ltd) and barium hydroxide ($Ba(OH)_2$, STREM CHEMICALS) were used as the Ti and Ba sources, respectively. The temperature was changed from 100 to 280 °C (100, 150, 200, 220, 240, 260, and 280 °C) under a fixed condition of Ba/Ti atomic ratio of 1.5 and molar number of barium ion of 0.015 molar. Obtained powders were filtrated, washed, and dried. The yield of $BaTiO_3$ particles was determined by molar number of titanium ion.

Their crystal structures were investigated by a conventional powder X-ray diffraction (XRD) method. The crystallite sizes were estimated from the $BaTiO_3$ (111) plane using Scherer's equation. The average particle sizes and shape were investigated by a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM).

Results and discussion

First, the distilled water was used as the solvent. Figure 1 shows a FE-SEM photograph of $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h. From Fig. 1, the shapes of the nanoparticles were aggregated elliptical spheres with an average size of around 150 nm. The XRD measurement revealed that the main product was perovskite-type $BaTiO_3$, and the crystallite size of 170 nm was estimated from the (111) peak. This result completely agreed with other reports about $BaTiO_3$ particles prepared using hydrothermal method [8–11]. In general, it was well-known that the $BaTiO_3$ particles can be prepared at room temperature, and the particle shape was always ellipse or sphere then. Figure 2 shows a schematic nucleation and particle growth mechanism for the $BaTiO_3$ particles prepared using water. In Fig. 2, the cluster growth is isotropic and the particle growth can be also regarded as isotropic owing to low crystallinity and contamination of impurity such as OH^- at low temperature below 200 °C. In addition, the cluster growth is also isotropic at higher temperature

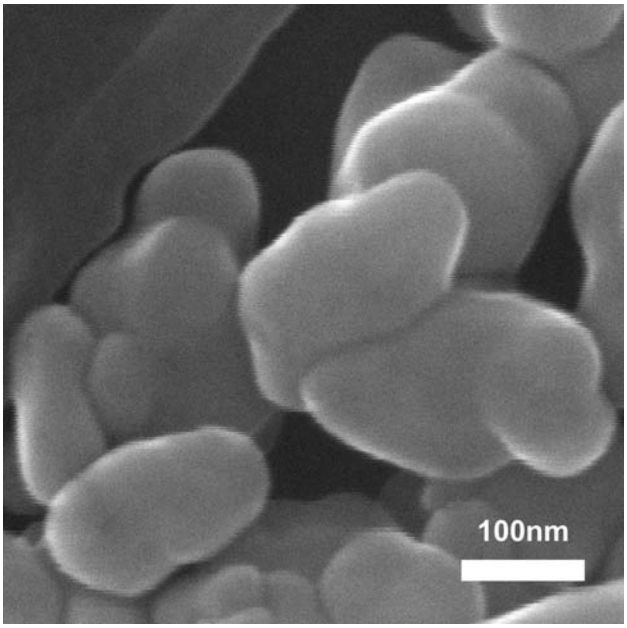

Fig. 1 A FE-SEM photograph of $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using water

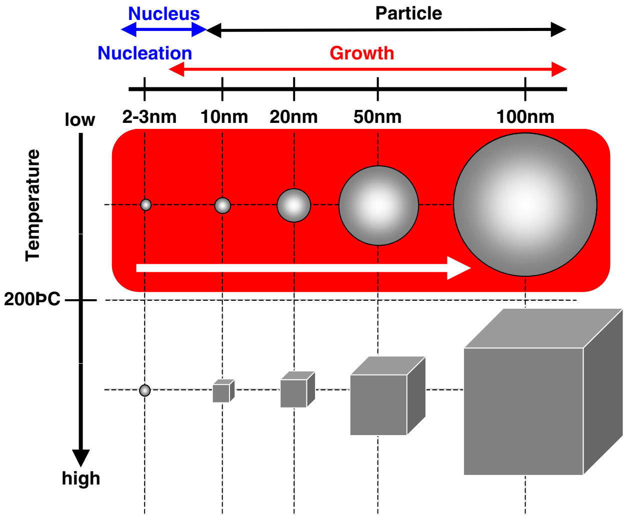

Fig. 2 Schematic nucleation and particle growth mechanism for $BaTiO_3$ particles prepared using water

over 200 °C. But when the particles grow over 2–3 nm, the facet growth can be dependent on the surface density in various atomic planes of $BaTiO_3$ lattice, i.e., the highest facet growth rate can be observed at the highest surface density. As a result of using water as solvent, the particle shape became always ellipse and sphere because of fast particle growth at low temperature.

Ethanol was used as solvent in next procedure. Figure 3 shows a TEM photograph of the $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h. The shape of the nanoparticles was almost sphere with an average size of around 10 nm according to Fig. 3. The XRD measurement evinced that the main product was perovskite-type $BaTiO_3$ and the crystallite size was estimated at 10 nm. This suggested that there was an increase of the nucleation number and a slight growth of $BaTiO_3$ below 200 °C when ethanol was used as solvent. At present, we cannot clearly explain the formation mechanism of the $BaTiO_3$ nanoparticles with sphere shape and size of 10 nm. It was known that both $Ba(OH)_2$ and TiO_2 have very low solubility in ethanol at room temperature. However, the increase of the nucleation number using ethanol may suggest a drastic increase of their solubilities at higher temperature.

Furthermore, the water and ethanol liquid solution system was used and investigated. Figure 4 shows a relationship between the crystallite size of the $BaTiO_3$ nanoparticles and the volume fraction of ethanol in water. A distinct plateau at around 55 nm was observed in the region between 40 and 80 vol.% ethanol (Fig. 4). Thus, the particle shape and sizes were investigated in this region. Figures 5 and 6 show FE-SEM photographs of the $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h in 60 vol.% ethanol and 80 vol.% ethanol–water solvent, respectively. The coexistence of large cubic-shape particles with round corner and small sphere particles is clearly seen in Figs. 5 and 6. The size of both particle types decreased with increasing ethanol volume fraction. These results revealed that first, small sphere-shape $BaTiO_3$ particles were formed, and then the particle growth mechanism changed from isotropic to anisotropic. This means that the particle growth mechanism transformation threshold can be shifted from

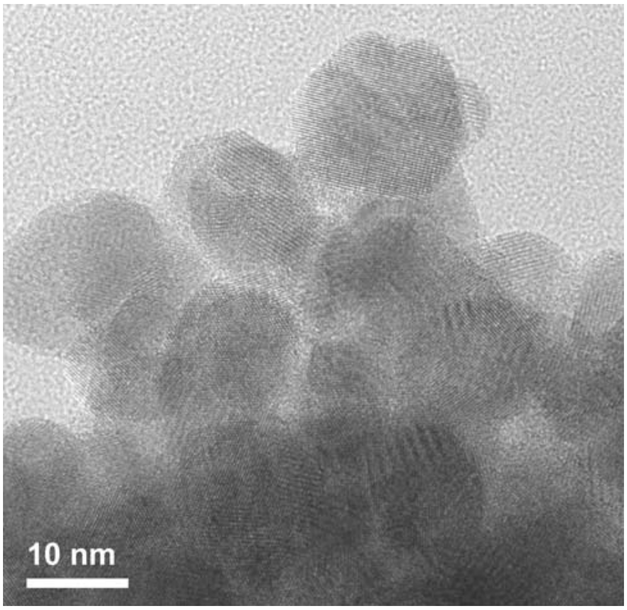

Fig. 3 A TEM photograph of $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using ethanol

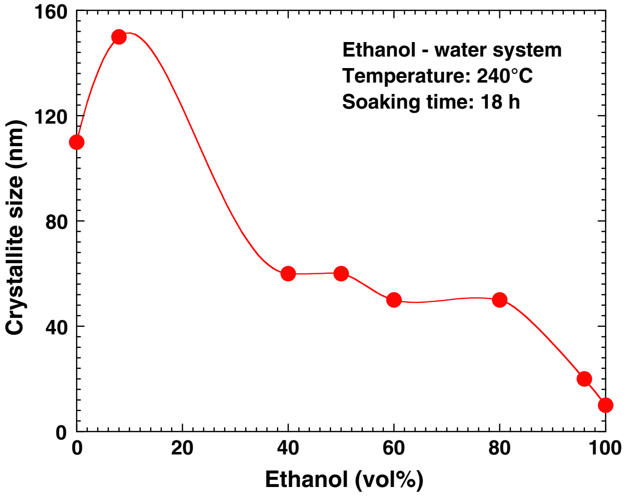

Fig. 4 Crystallite size dependence on volume fraction of ethanol for the $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using the water–ethanol system

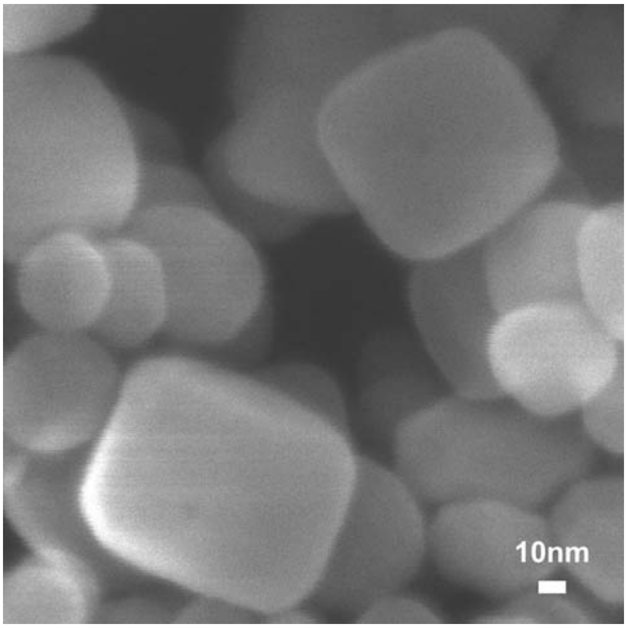

Fig. 5 A FE-SEM photograph of $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using 60 vol.% ethanol and 40 vol.% water

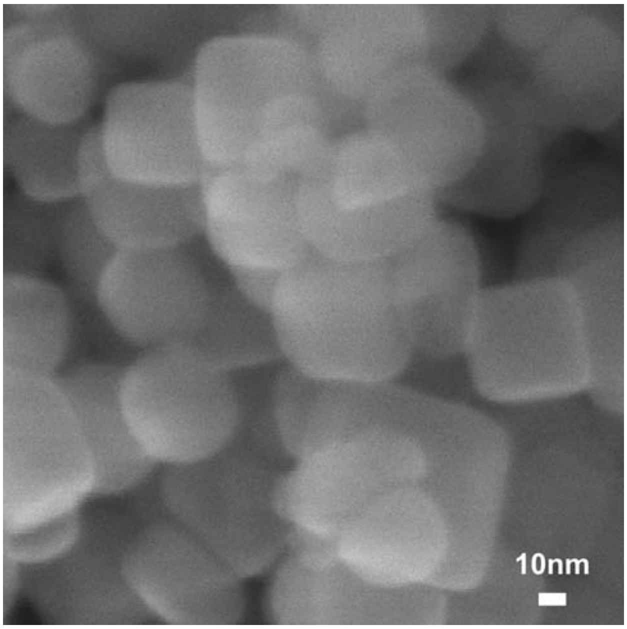

Fig. 6 A FE-SEM photograph of $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using 80 vol.% ethanol and 20 vol.% water

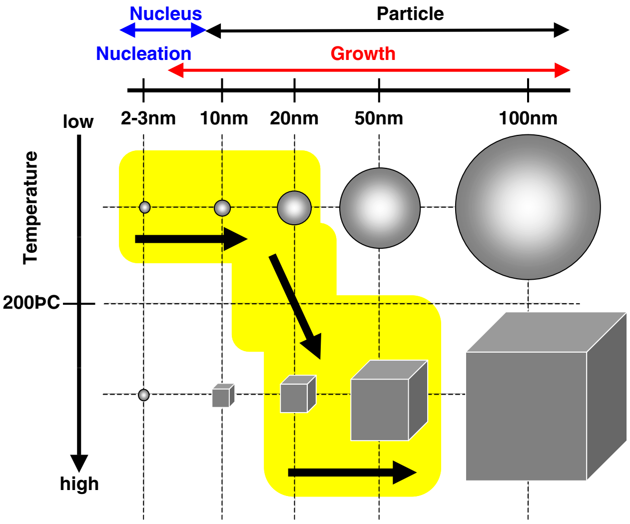

Fig. 7 Schematic nucleation and particle growth mechanism for $BaTiO_3$ particles prepared using ethanol–water system

the low temperature domain to the region above 200 °C by increase of the ethanol volume fraction, as shown in Fig. 7.

On the other hand, it is known that the increase of ethanol volume fraction in the water–ethanol system can make the solubilities of $Ba(OH)_2$ and TiO_2 very low at room temperature. The nucleation number increased with increasing ethanol volume fraction, and thus, the particle size decreased (Fig. 4). Therefore, the solubility of raw materials might be related to this particle size dependence. However, we cannot explain the origin of the particle size dependence. Moreover, the shape of the $BaTiO_3$ nanoparticles was not simply dependent on the ethanol volume fraction, in the ethanol–water solution system. We should investigate this particle shape formation mechanism in future research.

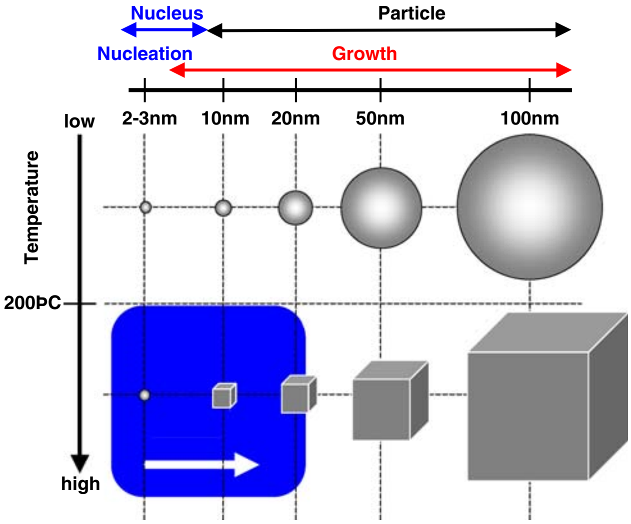

Fig. 8 Ideal schematic nucleation and particle growth mechanism for formation of $BaTiO_3$ nanocube particles

The above results and discussion can lead to the following hypothesis of formation of $BaTiO_3$ nanoparticles. The particle growth at low temperature below 200 °C is isotropic while the particle growth at high temperature above 200 °C is anisotropic and the facet planes with high surface density can grow preferentially. On the basis of preceding hypothesis, the formation of the $BaTiO_3$ nanocube particles with sizes below 20 nm can be expected if the nucleation and growth processes can be performed over 200 °C, as shown in Fig. 8.

The quest of a special solvent was evident for further advance. The solvent needs to have very low solubility of $Ba(OH)_2$ and TiO_2 below 200 °C to prevent the formation of $BaTiO_3$. This solvent should transit to a different solvent "X" with high solubility of $Ba(OH)_2$ and TiO_2 over 200 °C. Most of known organic solvents were investigated in this study. Accidentally, one solvent was found. This solvent was 2-methoxyethanol with a boiling point of 135.1 °C. When this solvent itself was heated up to 200 °C in the solvothermal reactor, there was no change of color, smell, and NMR spectra. On the other hand, the smell was different and the color changed from colorless to yellowish when the solvent was heated over 200 °C. The ^{1}H-NMR measurement indicated the change of NMR signals below and above 200 °C, but decomposed solvents were not identified yet. Although manuscripts related to thermal decomposition of 2-methoxyethanol under pressure over 200 °C were searched, but it was found that there were no reports about this.

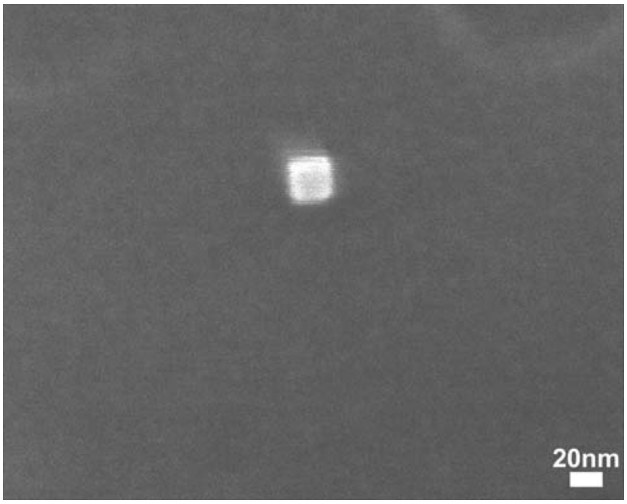

Fig. 9 A FE-SEM photograph of $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using 2-methoxyethanol

The 2-methoxyethanol was employed in further study procedures. Figure 9 shows a FE-SEM photograph of the $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using the 2-methoxyethanol solvent. Formed $BaTiO_3$ nanocube particles exhibit an average size of 23 nm and sharp-edged corner as can be seen in Fig. 9. Moreover, the XRD measurement revealed that the main product was perovskite-type $BaTiO_3$, and the crystallite size 29 nm was estimated. This is the first report of successful formation of the $BaTiO_3$ nanocube particles with sharp-edged corner and size below 30 nm. The TEM observation also confirmed the creation of the $BaTiO_3$ nanocube particles. This result supported the validity of the concept for the $BaTiO_3$ nanocube particles production.

The 2-methoxyethanol solvent was diluted by ethanol with volume fraction of 60 vol.% to reduce particle sizes from 30 nm with follow-up investigation. Figure 10 shows a TEM photograph of the $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using 40 vol.% 2-methoxyethanol and 60 vol.% ethanol. Sharp-edged corner $BaTiO_3$ nanocube particles of an average size of 12 nm are clearly visible on Fig. 10. The XRD measurement also proved the presence of perovskite-type $BaTiO_3$ as the main product. The crystallite size 15 nm was estimated. Therefore, our target to prepare the $BaTiO_3$ nanocube particles with sizes of around 10 nm was successfully achieved.

Conclusions

In this study, a condition of preparation of the $BaTiO_3$ nanocube particles was investigated. The nucleation and particle growth must be controlled over 200 °C for formation of the $BaTiO_3$ nanocube particles with sizes of around 10 nm. Special 2-methoxyethanol solvent was found for this purpose. Finally, the $BaTiO_3$ nanocube particles with a size of 12–15 nm and sharp-edged corner were successfully prepared using a mixture of 40 vol.% 2-methoxyethanol and 60 vol.% ethanol. This article is the first report about the preparation of the $BaTiO_3$ nanocube particles with sizes of around 10 nm. Moreover, the formation mechanism of the $BaTiO_3$ nanocube particles proposed in this study can be universal, and can be applied to other perovskite-type materials such as lead titanate, strontium titanate, calcium titanate, and so on. We will continue the study related to the formation of nanocube particles and develop a new ceramics processing with nanocube in the future.

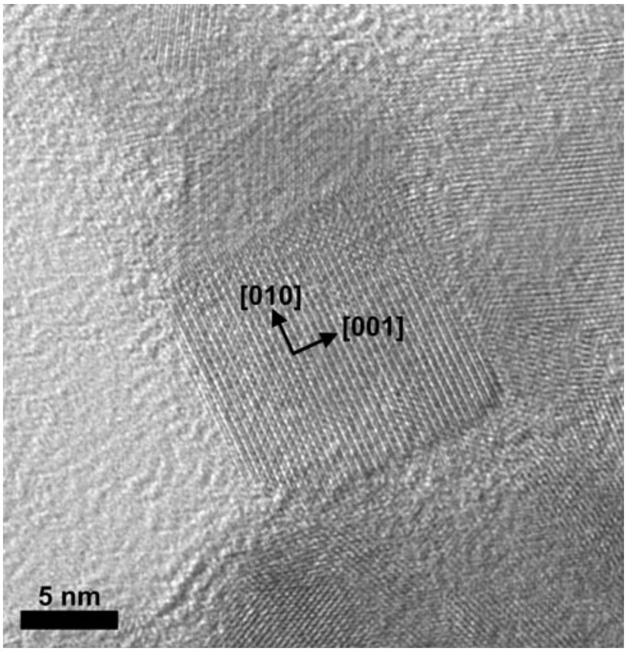

Fig. 10 A TEM photograph of $BaTiO_3$ nanoparticles prepared at 240 °C for 18 h using 40 vol.% 2-methoxyethanol and 60 vol.% ethanol

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