Enhanced dielectric response induced by controlled morphology in rutile TiO$_2$ nanocrystals

Minoru OSADA, Makoto KOBAYASHI, and Masato KAKIHANA

International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba, Ibaraki 305–0044, Japan

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2–1–1 Katahira, Aoba-ku, Sendai 980–8577, Japan

High-quality rutile TiO$_2$ nanocrystals have been synthesized by a simple hydrothermal treatment of a watersoluble titanium–glycolate complex at 200°C. The obtained samples were composed of rod- or whisker-like nanocrystals. The aspect ratios of these nanocrystals could be controlled by adding glycolic acid. Combined characterizations with X-ray diffraction, Raman scattering and high-resolution transmission electron microscopy revealed the formation of highly phase-pure and well-crystallized rutile nanorods/nanowhiskers with the c-axis orientation. Room-temperature dielectric measurements indicated that the permittivity for the rutile nanowhiskers is ~150 at 100 kHz, which is higher than that for the bulk rutile powder. These observations pave a way for morphological controlled rutile nanocrystals to find a broad class of technological uses.

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1. Introduction

Nanocrystalline ceramics have attracted considerable interest in recent years because of promising physical properties resulting from the effects of their small size and interfaces. In particular, exploring the dielectric properties of nanocrystals with a stable structure and controlled morphology has drawn great attention because they are necessary for novel electronic devices and energy storage systems. TiO$_2$ is a model oxide compound in this regard since it has three polymorphs of different symmetries: rutile, anatase and brookite, all of which can be described in terms of distorted TiO$_6$ octahedra with different symmetries or arrangements.

Numerous literature reports have concluded that rutile is an excellent dielectric material with high dielectric constant of ~120, which is the highest among simple oxides, while anatase exhibits much smaller dielectric constant of ~30. Brookite is theoretically predicted to be a promising dielectric comparable to rutile; nevertheless, its dielectric constant is still controversial due to the difficulties of materials synthesis. The dielectric properties of TiO$_2$ are strongly dependent on the polarization nature and thus are very sensitive to the interfaces, grain size and morphologies. In rutile TiO$_2$, the dielectricity is a directional property in which excellent properties occur only in the direction of the highly polar c-axis; it features high dielectric constant of 180 along the c-axis and 90 along the a-axis. Therefore, a detailed characterization on dielectric properties of rutile nanocrystals with controlled morphology is fundamentally important, while the prerequisites can be high-quality rutile synthesis.

Various synthetic strategies have been developed for controlled morphology of rutile TiO$_2$ nanocrystals, in which several preparation conditions including inorganic salts, organic substances, pH value, reaction time and temperature were investigated. However, dielectric properties of rutile TiO$_2$ nanocrystals with controlled morphology are still unexplored; a majority of research is limited to spherical nanoparticles and microspheres. Systematic investigations of morphological effects will be essential and significant for both the cognitive level and application fields, which may exemplify the property tailoring through materials synthesis and morphological control.

In this work, we utilized a simple hydrothermal treatment of a watersoluble titanium–glycolate complex to synthesize rutile TiO$_2$ nanocrystals with controlled morphology. This synthetic approach allows for excellent control of rutile morphology, and the aspect ratios of the rutile nanocrystals could be varied by adding glycolic acid to an aqueous solution of titanium–peroxo complex. Through this approach, we successfully synthesized high-quality rutile TiO$_2$ nanocrystals composed of c-axis oriented nanorods/nanowhiskers with the polarization induced by distorted TiO$_6$ octahedra. We performed a systematic investigation of the structure, spectral characteristics and dielectric properties of this unique polymorph.

2. Experimental section

Rutile TiO$_2$ nanocrystals with controlled morphology were synthesized by a hydrothermal treatment using a watersoluble titanium–glycolate complex according to previously described procedures. An aqueous solution of titanium–peroxo complex was prepared by dissolving 5 mmol titanium metal powder (98%, Wako Pure Chemical) in a cold solution containing 20 cm$^3$ H$_2$O (30%, Sanatoku Chemical) and 5 cm$^3$ NH$_3$ (aqueous) (28%, Kanto Chemical). Glycolic acid (7.5 mmol, Kanto Chemical) was added and the solution was heated on the hot plate set to 80°C to eliminate excess H$_2$O$_2$ and NH$_3$; this temperature was maintained until the entire mixture became a gel-like substance. This gel was re-dissolved in water to produce an aqueous solu-
tion of the peroxo–titanium–glycolate complex. The pH of this aqueous titanium complex solution was about 5.5. Then, 25 mmol glycolic acid was added into the titanium complex solution as an additive and the pH of the solutions changed to about 2.2. The total volume of the final aqueous solution was adjusted to 20 cm³ by adding distilled water ([Ti] = 0.25 mol/dm³) in Teflon vessel. This vessel was sealed in a stainless steel autoclave and heated in an oven at 200°C for 6–240 h. After the autoclave cooled to room temperature, the produced precipitate was separated using a centrifuge and/or filtration, washed with distilled water and dried at room temperature. For the discussion in our paper, we distinguish between the rod and whisker according the aspect ratio. We denote the nanoparticles with a rather small aspect ratio of 2–5 as a nanorod, whereas the nanoparticles with a higher aspect ratio of >20 are called as a nanowhisker. Complementary data were obtained from a commercially available bulk rutile powder (~1 μm particle size).

The phase purity of the final products was examined by X-ray diffraction (XRD) (Bruker AXS, D2 Phaser, CuKα radiation). Morphologies of the final products were observed by transmission electron microscopy (TEM) (Hitachi H7650 and Carl Zeiss, LEO912). Raman spectra were obtained on a micro-Raman spectrometer (Horiba-Jobin-Yvon T64000) with an excitation line of 514.5 nm. The dielectric measurements were carried out in a frequency range from 50 Hz to 1 MHz and at an oscillation voltage of 0.5 V using a precision LCR meter (Agilent 4980).

3. Results and discussion

Figures 1 and 2 show XRD patterns and TEM images of the samples prepared with given pH values at 200°C. The product obtained with pH = 5.5 was pure rutile phase composed of the rod-like nanocrystals. From the statistical investigation of TEM images [Fig. 2(c)], the average width and length of the rod-like nanocrystals were 48.6 and 136 nm, respectively; the average aspect ratio attained to ~2.9. After the pH value was adjusted to 2.2 by adding glycolic acid, the product was still pure rutile phase, while the crystal length grew up to form the whisker-like nanocrystals. The average width (49.1 nm) of the whisker-like nanocrystals was almost unchanged from the nanorods, while the average length grew up to be micro-scale (1188 nm) [Fig. 2(d)]. The average aspect ratio attained to ~28.5.

Figure 3 shows high-resolution TEM images of the rod- and whisker-like nanocrystals. The image of Fig. 3(a) clearly indicates the formation of well-crystallized rutile nanorod grown in the [001] direction. The lattice fringes shown in the HRTEM image were 0.29 and 0.325 nm, corresponding to the distances of (001) and (110) lattice planes, respectively. The observed (110) lattice spacing (0.325 nm) between adjacent lattice planes was slightly larger than typical value (0.32 nm) of rutile TiO₂, which indicates the tensile strain along the [110] direction. The side facets of these nanorods were (110), (-110), (1–10) and (-1–10), a crystal habitus being persistent in the nanowhiskers [Fig. 3(b)].

The formation of the rod-like shape should be related to the surface energy difference of the lattice planes. In the crystal with an isotropic surface energy, the obtained crystal should be nearly spherical, while if the surface energy is anisotropic, the energy-minimizing shape could be formed by the limiting planes of the possible lowest surface energy. In rutile TiO₂, the oxygen atoms predominate on the (001) plane, while both the (110) and (111) planes are titanium rich. Therefore, the (110) and (111) planes provide preferential adsorption sites of glycolic acid molecules. Facets with chelated Ti atoms apparently have a lower surface energy, so they tend to develop further during particle growth. As indicated by theoretical studies, among (100), (010), (001), (110), (011) and (111) planes of rutile TiO₂, the (001) plane holds the smallest surface formation energy. This calculation also supports that rutile crystal prefer growth along the [001] direction to give the non-spherical morphology.

Such a morphological control can have a strong impact on phonon and dielectric properties. Raman spectra are effective to investigate the vibration behaviors of the chemical bonds and local structures. Figure 4 compares the Raman spectra of the rod-/whisker-like rutile nanocrystals and bulk sample. Rutile TiO₂ is tetragonal with space group P4/mmm, which yields 4 Raman-active modes ((A₁g, B₁g, B₂g modes) or along the c-axis (E₂g mode). Raman spectrum of the bulk sample revealed 4 vibration bands in the range of 100–900 cm⁻¹, which can be assigned to the first-order modes of B₁g (143 cm⁻¹), E₂g (447 cm⁻¹), A₁g (612 cm⁻¹) and B₂g (826 cm⁻¹), respectively. In addition, second-order scattering features were observed; the most prominent one at ~240 cm⁻¹. In the nanorods/nanowhiskers, on the other hand, the E₂g and A₁g modes as well as the second-order mode at ~240 cm⁻¹ were the major features while B₁g and B₂g modes were extremely weak or absent. The size-dependent modifications of the Raman spectra were clearly seen for the E₂g and A₁g modes: increase redshift in the Raman frequency, asymmetric low-frequency broadening and reduced peak intensity.

These changes are consistent with phonon confinement effects from the 1D rod-like nanocrystals. According to the phonon confinement model, the nature of phonon dispersion away from the Brillouin zone center determines the nature of modification in the Raman line shape as a function of crystalline size. A negative phonon dispersion away from the zone center would result in asymmetric low-frequency broadening and redshift of Raman frequency, along with a reduction in intensity with decreasing particle size. In our nanorod/nanowhisker cases, because of the dimensional constrain along the direction (a, b) axis perpendicular to the rod axis, the phonon confinement effects are more pronounced in the in-plane A₁g mode. For the A₁g modes...

Fig. 1. XRD patterns of the samples prepared with given pH values at 200°C. Vertical bars in the bottom layer denote the standard data for rutile (JCPDS: No. 21-1272).
mode, inelastic neutron scattering measurements and theoretical modeling gave a flat branch along [110], both lying in the plane of the Ti-O stretch, with oxygen vibrations defining the mode.\textsuperscript{18),19} Thus, the phonon dispersion is consistent with the observed redshifts, asymmetric low-frequency broadening and reduced peak intensity of the $A_{1g}$ mode.

The dielectric properties of the rutile TiO$_2$ nanocrystals were investigated by impedance measurements, which were performed on the pellet obtained by pressing the mixture of as-prepared rutile powders with 4\% PVB [poly(vinyl butyral)] and heating between 200$^\circ$C, and then calcining at 450$^\circ$C to sufficiently eliminate the rudimental PVB. It is noted that the pellet maintained the pure rutile phase without microstructural collapse or apparent morphological and scale changes. Dielectric permittivity ($\varepsilon'$) and loss tangent (tan $\delta$) as a function of frequency at room temperature for the rutile TiO$_2$ nanocrystals are shown in Fig. 5. Complimentary data obtained from the bulk rutile powder are also plotted. In the rutile TiO$_2$ nanorods and nanowhiskers, low frequency permittivity values ($\varepsilon'$) were 150 and 300, and $\varepsilon'$ decreased with increasing the frequency. Dielectric permittivity of the nanowhiskers with a high aspect ratio was higher than that of nanorods; the nanowhiskers exhibited a large permittivity of $\approx$150 (at 100 kHz), which was higher than that of the bulk rutile powder. For the loss tangent, a Debye-like relaxation peak was observed at low-frequency region, and the peak shifted towards lower frequency on reduced aspect ratio (i.e. nanorods). These observations indicate the different microstructural characteristics of nanocrystals cause different dielectric responses, particularly for lower frequency region. Our samples are composed of interfaces with a large volume faction and nano-TiO$_2$ grains. The polarization relaxation in the interfaces constructed by tiny rutile nanorods/nanowhiskers possesses a shorter relaxation time than that of the bulk rutile. In this regard, surface dipoles for the nanocrystals may play a predominant role in determining the low-frequency dielectric responses.

It is well documented that high permittivity for bulk rutile TiO$_2$ arises from the very strong internal electric fields, causing strong deformation of electron shells and polarization of both Ti$^{4+}$ and O$^{2-}$ ions. Samara and Peercy reported that the high static dielectric constant of single crystal rutile is due to both large electronic polarization and ionic polarization due to non-polar optical vibrations.\textsuperscript{7} Rutile TiO$_2$ is an incipient ferroelectric material,\textsuperscript{18),20} and it has been shown via ab initio simulations that a ferroelectric distortion can be induced by either negative pressure or tensile [110]-oriented strain.\textsuperscript{21} In this regards, our nanocrystals are of the tensile strain condition along the [110]...
direction. Since the equatorial Ti–O bond length increases under the tensile [110] strain, the short-range repulsion between these ions is reduced. In such a case, a large polarization emerges in the [001] direction, which further enhances the electronic polarizability. Although further investigations are necessary for full understanding the influence of strain on dielectric/ferroelectric properties, our work opens up new possibility of morphological control and strain engineering in high permittivity TiO₂ nanocrystals.

4. Summary

Rod- and whisker-like rutile TiO₂ nanocrystals were synthesized by a simple hydrothermal treatment of a watersoluble titanium–glycolate complex at 200°C. The aspect ratios of these nanocrystals could be controlled by adding glycolic acid; at reduced pH condition, rutile crystal prefer growth along the [001] direction to give the whisker-like morphology with a high aspect ratio. Such morphological controlled rutile nanocrystals exhibited a robust dielectric response of ~150, which was higher than that of the bulk rutile powder. These observations provide a novel strategy of morphological control in creating new dielectric materials.

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References