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

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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 morphologically 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. However, dielectric constant of rutile TiO$_2$ nanocrystals with controlled morphology is 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$_2$ (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. Complimentary 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 nanocrystals. The average width (49.1 nm) of the whisker-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 nanocrystals. The average width (49.1 nm) of the whisker-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 nanocrystals. The average width (49.1 nm) of the whisker-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 nanocrystals. The average width (49.1 nm) of the whisker-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 nanocrystals.

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.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°C, and then calcining at 450°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 $\varepsilon'$ = 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 Percey 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.7) Rutile TiO$_2$ is an incipient ferroelectric material,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.21) In this regards, our nanocrystals are of the tensile strain condition along the [110]

![Fig. 2. (a, c) TEM images and (b, d) distribution histograms of the rod- and whisker-like rutile nanocrystals. (c-1) the width and (c-2) length of the nanorods. (d-1) the width and (d-2) length of the nanowhiskers.]
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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