

Characterization of Raman Spectra of Size-Selected TiO₂ Nanoparticles by Two-Dimensional Correlation Spectroscopy

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Nanometer-sized materials have intensively studied due to their unique physical and chemical properties as well as their great potential of technological applications.¹⁻⁵ Despite many studies on the structure-property relations of nanoparticles using the various characterization techniques, such an understanding is still to be answered. Therefore, we have recently explored the relationship between the size and structure of size-selected TiO₂ nanoparticles, which are prepared via a hydrolysis method with Ti[OCH(CH₃)₂]₄ as the starting material, by X-ray absorption spectroscopy (XAS).⁶ Analysis of the XAS of the samples with an average particle size of ~30 nm (sample A), ~12 nm (sample B), and ~7 nm (sample C) demonstrated that samples A and B have an anatase structure, whereas sample C has a structure very similar to that of the TiO₂ II phase. The TiO₂ II phase generally arises only under high-pressure conditions. This difference can be attributed to size-induced radial pressure within the smaller nanoparticles, which plays an important role in the phase of TiO₂ nanoparticles in sample C. In addition, we have studied the relationship between the particle size and change of Raman bands of TiO₂ nanoparticles, sample A and sample B.⁷ The obtained Raman spectra showed the broadening and shift of Raman bands with decreasing particle diameter. The origin of Raman shifts can be attributed to the effect of smaller particle size and it affects the force constant and vibrational amplitudes of the nearest neighbor bond.

In this study, in order to analyze the vibrational modes of size-selected TiO₂ nanoparticles and to the shift of Raman bands of TiO₂ nanoparticles with particle size, we have applied two-dimensional (2D) correlation spectroscopy to the particle size-dependent Raman spectra of TiO₂ nanoparticles. Generalized 2D correlation spectroscopy has been applied extensively to the analysis of spectral data sets obtained during the observation of a system under some external perturbation.⁸⁻¹⁰ Because of the wide range of applications of this technique, it has become one of the standard analytical techniques for interpreting various types of spectroscopic data. The details of this technique are described elsewhere,⁸⁻¹⁰ so no further description is given here.

Experimental Section

TiO₂ nanoparticles were prepared via a hydrolysis method using titanium isopropoxide (Ti[OCH(CH₃)₂]₄, Aldrich, 99.999%) as the starting material without further purification. The Ti[OCH(CH₃)₂]₄ solution was added to 200 mL 2-propanol at room temperature with vigorous stirring and then 800 mL the deionized water was added to the solution. The reaction conditions were maintained for 1 h to reach equilibrium of reactions, hydrolysis and particle formation. Sample A was obtained only by standing the resulting solution without stirring and the precipitated particles were separated from the solution by filtration and repeatedly washed with deionized water, whereas samples B and C were obtained by adjusting the stirring rate of the resulting solutions to 200 and 2000 rpm, respectively, and the precipitated particles were dried with a freeze-drier. Finally, the preparation of three size-selected samples of the TiO₂ nanoparticles was then completed by heating the precipitated particles in each sample at 450 °C for 1 h.

FT-Raman spectra were obtained at room temperature using a Bruker FRA 106/S FT-Raman spectrometer equipped with an InGaAs detector. The radiation from an Nd-YAG laser (1.5 W) was used as the excitation source.

2D correlation analysis was performed using an algorithm based on the numerical method developed by Noda.⁹ The 2D correlation analysis was carried out after baseline correction of the Raman spectra. A subroutine named KG2D¹¹ written in Array Basic language (GRAMS/386; Galactic Inc., Salem, NH) was employed for the 2D correlation analyses.

Results and Discussion

Figure 1 shows the Raman spectra of three types of TiO₂ nanoparticles and the reference spectrum of anatase TiO₂. Bulk anatase has a tetragonal structure (space group *I4₁/amd*) containing twelve atoms per unit cell with lattice parameters *a* = 3.784 Å and *c* = 9.514 Å.¹² According to factor group analysis, anatase has six Raman active modes (*A_{1g}* + 2*B_{1g}* + 3*E_g*). Ohsaka reported the Raman spectrum of an anatase single crystal that the six allowed modes appear at 144 cm⁻¹ (*E_g*), 197 cm⁻¹ (*E_g*), 399 cm⁻¹ (*B_{1g}*), 513 cm⁻¹ (*A_{1g}*), 519 cm⁻¹ (*B_{1g}*), and 639 cm⁻¹ (*E_g*).¹³ The main spectral features of samples A (~30 nm) and B (~12 nm) are closely similar to those of the reference TiO₂, which mean that the

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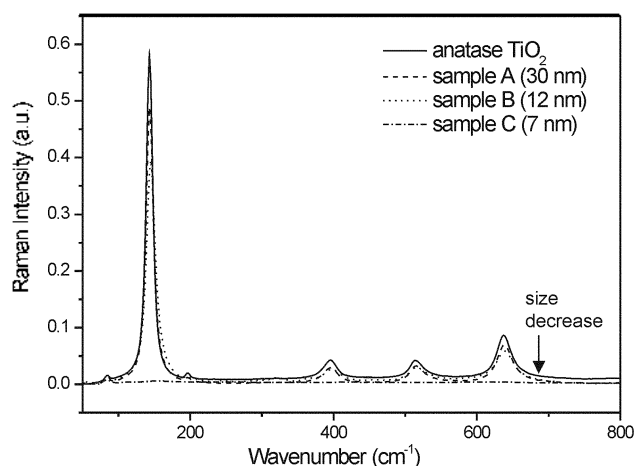


Figure 1. Raman spectra of size-selected TiO_2 nanoparticles.

prepared samples A and B possess a certain degree of long-range order of the anatase phase. However, the spectrum of sample C (~ 7 nm) is quite different from the others, showing the band broadening with decrease in intensity. This difference in Raman spectra of TiO_2 nanoparticles can be attributed to the effect of smaller particle size and it affects the force constant and vibrational amplitudes of the nearest neighbor bond. Due to its ambiguous feature, however, no detailed information about the structure of sample C can be derived from the conventional 1D Raman spectra.

To elucidate the Raman spectra of size-selected TiO_2 nanoparticles in greater detail, we applied 2D correlation analysis to two sets of data for the particle size-dependent Raman spectrum. The first set was constructed from spectra shown in Figure 1 without sample C and the second set from all spectra in Figure 1. As far as we know, no single crystals of TiO_2 II phase have been obtained. The high pressure phase, TiO_2 II, is believed to have isostructure with the orthorhombic $\alpha\text{-PbO}_2$ phase (space group $Pbcn$).¹⁴⁻¹⁶ Sekiya

et al. studied the pressure-induced phase transition from anatase to TiO_2 II using Raman spectroscopy, showing that the new Raman bands were mainly observed between 300 and 700 cm^{-1} when the TiO_2 II phase was formed.¹⁵ Therefore, in this study, we have focused on the comparison of 2D correlation spectra for first set with those for second set in the spectral region of 300–700 cm^{-1} .

The synchronous and asynchronous 2D Raman correlation spectra from the first data set are displayed in Figures 2(a) and 2(b), respectively. Synchronous cross peaks yield the bands at 638, 515, and 397 cm^{-1} , while the asynchronous cross peaks show those at 641, 517, and 398 cm^{-1} . Bands detected in 2D correlation spectra strongly support that all bands shift into a higher frequency with decreasing the particle size. This band shift to higher frequency can be explained by the effect of smaller particle size on the force constants. When the particle size decreases to the nanometer scale, a volume contraction occurs within the nanoparticles and leads to increases in the force constants as a result of the decreases in the interatomic distances. Consequently, the Raman bands shift towards a higher frequency due to the increasing force constants. In this study, therefore, the band shift of TiO_2 nanoparticles suggests that size-induced radial pressure in TiO_2 nanoparticles increases as the particle size decreases, and these results in a volume contraction. In addition, the synchronous 2D correlation spectrum has all positive cross peaks at (638, 515), (638, 397), and (515, 397) cm^{-1} , which reveals that intensity of these bands decrease together with decreasing the particle size.

Figure 3(a) and (b) display synchronous and asynchronous 2D correlation spectra from the second data set, respectively. The synchronous 2D correlation spectrum is similar to that from the first data set. However, bands at 343, 393, 410, 439, 472, 483, 510, 524, 618, 634, and 649 cm^{-1} that are not readily noticeable in the 1D spectra of Figure 1 are clearly observed in the asynchronous 2D correlation spectrum

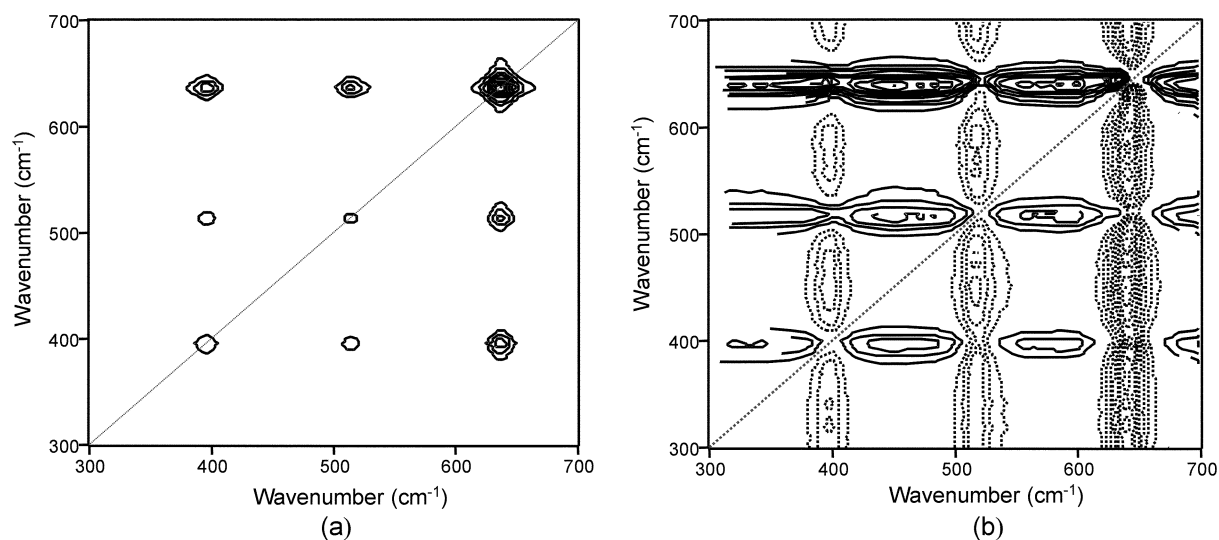


Figure 2. Synchronous (a) and asynchronous (b) 2D Raman correlation spectra generated from the first data set of the particle size-dependent Raman spectra of TiO_2 nanoparticles in the spectral region 300–700 cm^{-1} . Solid and dotted lines represent positive and negative cross peaks, respectively.

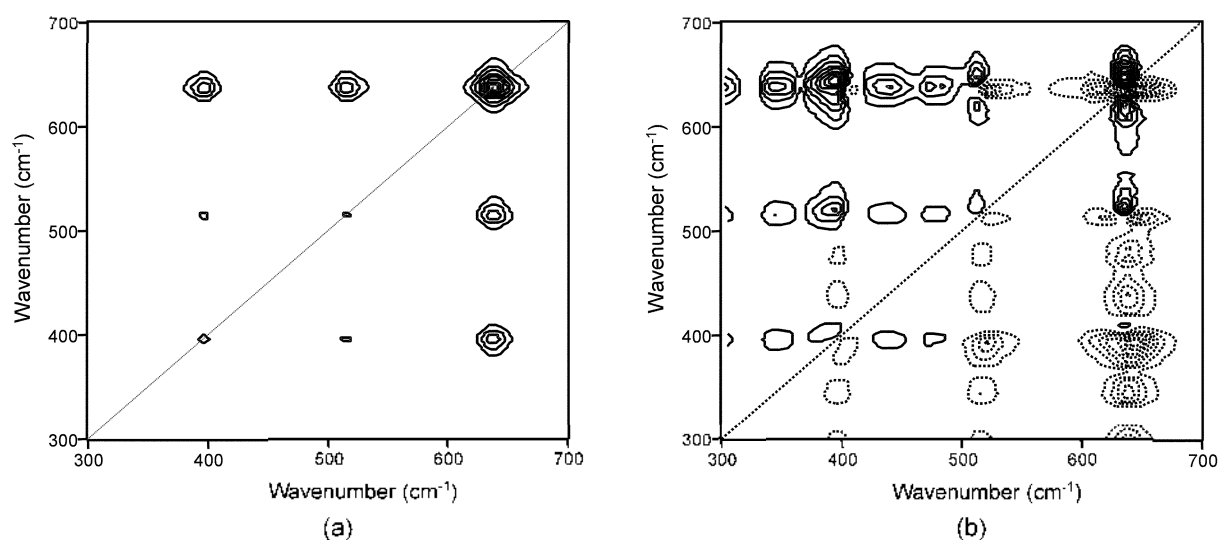


Figure 3. Synchronous (a) and asynchronous (b) 2D Raman correlation spectra generated from the second data set of the particle size-dependent Raman spectra of TiO_2 nanoparticles in the spectral region 300–700 cm^{-1} . Solid and dotted lines represent positive and negative cross peaks, respectively.

[Figure 3(b)], showing that the 2D correlation spectrum yields greater resolution than the conventional 1D spectra. These observed bands in the asynchronous 2D correlation spectrum are considerably similar to those of TiO_2 II phase reported by Lagarec and Desgreniers.¹⁵ This implies that sample C has a structure very similar to that of the TiO_2 II phase, which generally arises only under high-pressure conditions. However, the frequencies of the bands detected from 2D correlation analysis is not exactly that of the TiO_2 II phase observed at high-pressure condition.¹⁵ This difference can be understood that no single crystals of TiO_2 II have been obtained and the high-pressure phase, TiO_2 II, is a metastable quench product obtained only on release of high pressure,^{14,16} and sample C attributed to size-induced radial pressure within the smaller nanoparticles is not the high-pressure phase. Therefore, it can be concluded that the phase transition from anatase to TiO_2 II occurs with the decrease in the particle size of TiO_2 . Moreover, TiO_2 II structure is more favorable than the anatase structure for TiO_2 particles approximately 7 nm in size. It is a good agreement with our previous XAS results.⁶

Conclusion

In this study, we demonstrated the use of 2D correlation spectroscopy in characterization of Raman spectra of size-selected TiO_2 nanoparticles. The 2D correlation analysis clearly showed that all Raman bands shift into a higher frequency with decreasing particle diameter of TiO_2 nanoparticles. The origin of Raman bands shift can be attributed to the effect of smaller particle size and it affects the force constant.

The observed bands from 2D Raman correlation spectra revealed that sample C is very similar to high-pressure phase, TiO_2 II, which is not clearly observed in conventional 1D spectra. The size-induced phase transition from anatase to TiO_2 II is successfully explored by 2D Raman correlation analysis.

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