TWO-DIMENSIONAL CORRELATION ANALYSIS OF RAMAN SPECTRA OF SIZE-SELECTED TiO_2 NANOPARTICLES

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Abstract: This paper demonstrates the use of two-dimensional (2D) correlation analysis for characterizing the vibrational modes of size-selected TiO_2 nanoparticles and the shift of Raman bands of TiO_2 nanoparticles with particle size.

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 TiO_2 nanoparticles, three size-selected samples of TiO_2 nanoparticles prepared via a hydrolysis method that uses $Ti[OCH(CH_3)_2]_4$ as the starting material, by X-ray absorption spectroscopy (XAS).[1] 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 TiO_2 II phase, which 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 TiO_2 nanoparticles in sample C. In addition, we have studied the relationship between the particle size and change of Raman bands of TiO_2 nanoparticles, sample A and sample B.[2] 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.

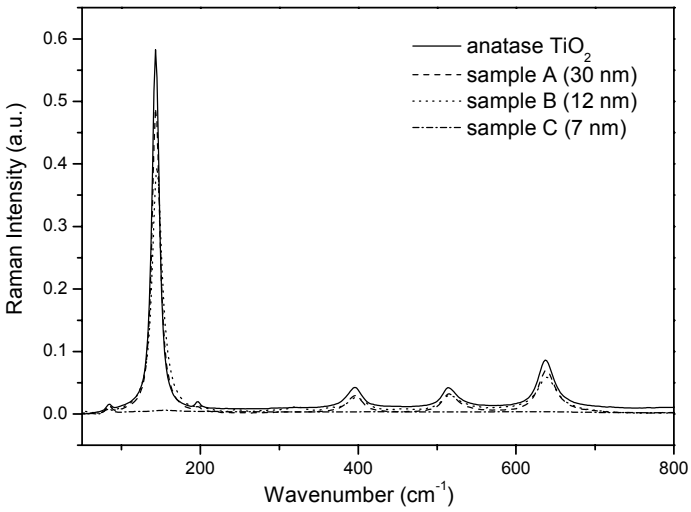

Fig. 1. . Raman spectra of (a) reference, (b) samples A, (c) sample B, and (d) sample C.

In order to analyze the vibrational modes of size-selected TiO_2 nanoparticles and the shift of Raman bands of TiO_2 nanoparticles with particle size, we have applied two-dimensional (2D) correlation analysis to the particle size-dependent Raman spectra of TiO_2 nanoparticles.[3] 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(b)], showing that the 2D correlation spectrum yields greater resolution than the conventional 1D spectra. 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. 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.

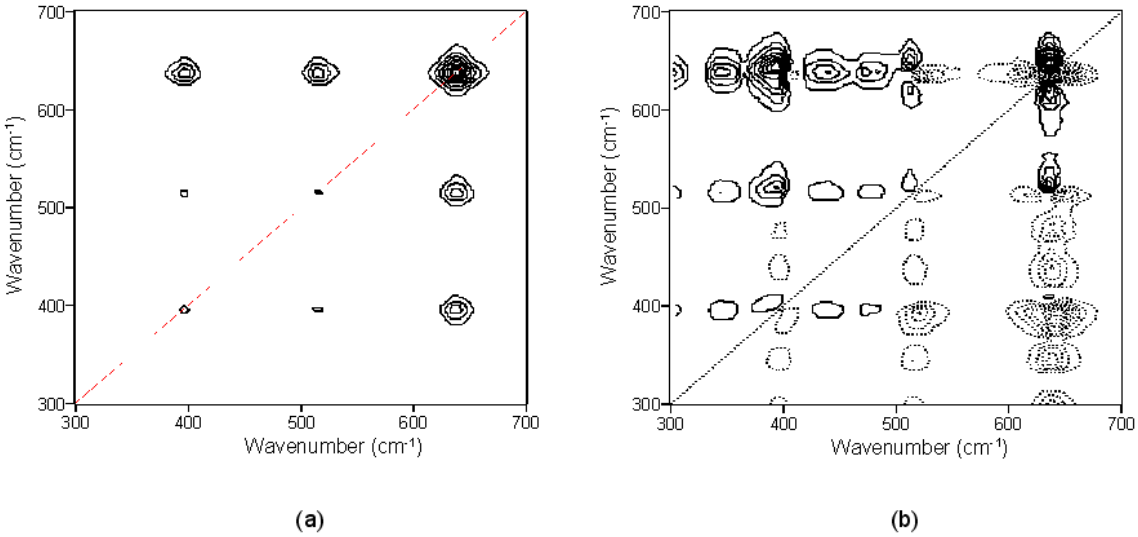

Fig. 2. Synchronous (a) and asynchronous (b) 2D Raman correlation spectra from the particle size-dependent Raman spectra of TiO_2 nanoparticles. Solid and dotted lines represent positive and negative cross peaks, respectively.

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References:

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