

Chemical Band Structure of V-doped TiO₂ Nanopowder

Synthesized by Aerosol-Assisted Chemical Vapor Synthesis

H. Park¹, J.P. Ahn¹, Y.S. Cho², H. Sieger², H. Hahn², J.K. Park¹

¹Nano-Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131,
Cheongryang, Seoul, 130-650, Korea

²Department of Materials Science, Technical University Darmstadt, 64295 Darmstadt, Germany

Proceeding to the International Congress of Nanotechnology

November 7-10, 2004, San Francisco

Abstract

Aerosol-assisted chemical vapor synthesis (AACVS) was applied to the manufacturing of V-doped TiO₂ (titania) nanopowders, Ti_{1-x}V_xO₂, with the vanadium of ~10 atomic percent. The nanopowder was characterized using transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements and its various physiochemical properties were investigated by UV-vis, FTIR, and Raman spectroscopies.

The titania nanopowders were about 7 nm in average diameter, 200~240 m²/g of specific surface area, and round in shape. The increase of V contents in the particle did not make the change of particle size, but led to the lattice distortion due to the formation of Ti_{1-x}V_xO₂ solid solution. When heat-treated over 600°C, a phase transition from anatase to rutile occurred and a vanadium oxide phase, V₂O₅, also was precipitated from the V-doped titania nanopowder. FTIR and Raman measurements revealed that the V-doped titania nanopowders had much more bridging Ti-O-V

bond than V-O-V bond. Accordingly, the titania nanopowder showed the red shift behavior as well as a large visible absorption in UV-vis spectra due to the formation of many bridging Ti-O-V bonds with the fully solid solution of $Ti_{1-x}V_xO_2$. However, the heat-treated V-doped titania nanopowder showed neither the red shift nor the large absorption of visible light.

Keywords: TiO_2 , $Ti_{1-x}V_xO_2$, Ti-O-Ti, Ti-O-V, Bridging Band, Doping, Bandgap energy, Visible absorption, AACVS

Introduction

TiO_2 containing donor-like oxygen vacancies has been widely used in photocatalyst, solar cell, and gas sensor, since Fujishima and Honda demonstrated the photoelectrical properties from TiO_2 in water [1]¹. The titania in photocatalyst has a noble photonic property which under light irradiation with energy larger than the bandgap energy of 3.2 eV, an electron in valence band moves up to conduction band leaving a hole in valence band, and then each electron and hole acts as a chemically strong reductant and oxidant. Recently an effective method to generate the free electron is known to control the bandgap energy of semiconductor using doping elements. In a fundamental research, the bandgap of the semiconductors can be altered by mixing two semiconductors with different bandgap energies. For example, the representative method substitutes various transition metals for titanium cation in titania and then changes the chemical bonding force between the cation and anion [2,3]²³.

The gas condensation process containing AACVS method for molecular doping has proven to be effective in preparing new catalysts [4]⁴. The foreign element of ~10% can be easily doped into the lattice of particle by the process. The AACVS can use variously the mixtures of two or more precursors and the reaction rate forming a particle is less than a few micro second. Therefore, it can plainly make the new catalysts having diverse structures.

Vanadium among transition metals has one more additional valence electron than titanium, while

their ionic radius is very close each other [5]⁵. Therefore, the vanadium doped in TiO₂ matrix can exist as a solid solution. Extra electron is known to act as a n-type dopant by donating an additional electron to the conduction band [6,7]⁶⁷.

TiO₂ catalysts can absorb the ultraviolet of 3~5% among solar beam that can reach the earth. Therefore, it is necessary to develop a photocatalytic system which can be applied under visible or solar light irradiation. In this paper, we manufactured the V-doped titania nanopowder using AACVS method which combines both an aerosol generator and a chemical vapor synthesis method (CVS). We also discussed the chemical mixing state of the V and Ti cations in V-doped titania nanopowder and the effect of vanadium on photo absorption in UV-vis range.

Experimental Procedure

AACVS was used for the synthesis of V-doped titania nanopowder. The mixtures of titanium tetra isopropoxide and vanadium oxitetra isopropoxide were prepared under argon glove box and were fed to an evaporator at a flow rate of 25 ml/h with oxygen gas of 2000 sccm. The evaporated precursor was supplied into a furnace kept at 1250°C and was thermally decomposed. Then TiO₂ nanopowder was synthesized and was collected by thermophoretic method. The pressure of reaction chamber was controlled at 10 mbar using throttle valve. On the other hand, the V-doped titania nanopowder was heat-treated at several temperatures in air.

The crystal structure of TiO₂ nanopowder and the lattice distortion by V-doping were measured by X-ray diffraction (Philips XRD 1830 using Cu K_α radiation) and the microstructure was observed by TEM (FEI Tecnai G²). The thermal stability and the precipitation of vanadium in titania were investigated by differential scanning spectrometer (DSC, Netzsch STA 409PC). The measurement of specific surface area was performed by BET (Perkin-Elmer, Autosorb-3). The chemical bonding structure of V-doped TiO₂ nanopowder was measured by FTIR (Thermo Mattson, IR300) and Raman (Labram, Dilor Instruments S.A.) spectroscopes and photo absorbance was done by UV-vis spectrometer (Varian, Cary300).

Results

1. Characterization of catalysts

The X-ray diffraction patterns of titania with the content of V dopant are given in Fig. 1. The titania nanopowder is anatase containing ~5% rutile. As a function of V contents, the full width half maximum (FWHM) of anatase (101) peak decreases slightly, while the intensity increases. It means that the particle of titania grew a little by increasing V contents. In particular, the peak position shifts to the left with the contents of V dopant, indicating that the lattice distortion is involved in titania matrix due to the formation of a solid solution. From the X-ray diffraction measurement, we could not find any clue on the being of vanadium oxides such as V_2O_5 or VO_2 .

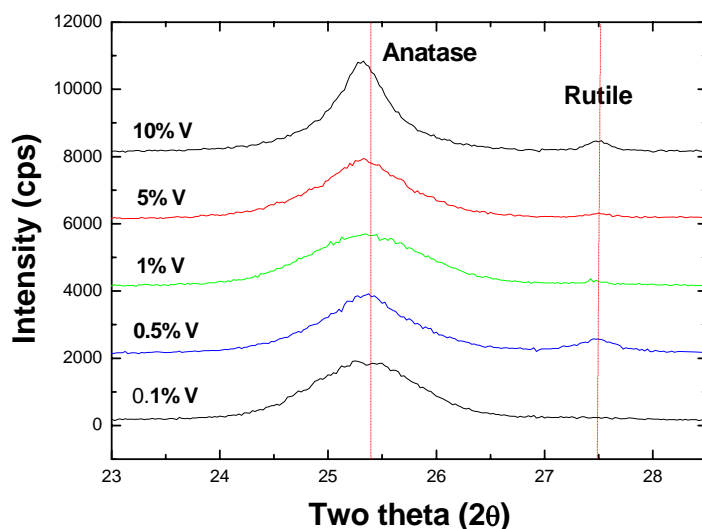


Fig. 1. Anatase (101) and rutile (110) peaks in X-ray diffraction pattern of V-doped titania nanopowders.

The 0.5%V-doped titania nanopowder in TEM observation of Fig. 2 has a chain-like round shape and is about 7 nm in diameter. The particle size is corresponding to the specific surface area of

200-240 m²/g measured by BET. Unlike the result shown in X-ray diffraction, the particle size with increasing V contents seems to be not changed in TEM observation (not shown here). We can not prove the being of V in the observation of titania nanopowder using TEM as well as X-ray diffraction. In analysis using energy dispersive X-ray (EDX), inductively coupled plasma (ICP), and X-ray photoelectron spectroscopy (XPS), however, it is proven that the atomic ratios of Ti and V elements agreed with the compositional ratio of precursor mixture.

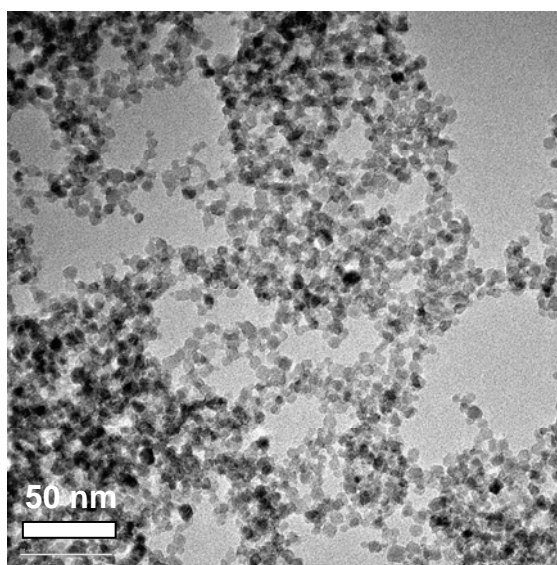


Fig. 2. TEM micrograph of 0.5V-doped titania nanopowder.

2. The precipitation, grain growth and phase transition in catalysts

Fig. 3 shows the DSC spectrum of 5%V-doped titania nanopowder. Several peaks are observed in the spectrum due to the combinations of the precipitation of vanadium, the grain growth of titania particles, and the phase transition from anatase to rutile. The precipitation and phase transition gives rise to an endothermic reaction while the grain growth causes an exothermic reaction. In general, these phenomena can take place at the same temperature because it is related to mass

transport.

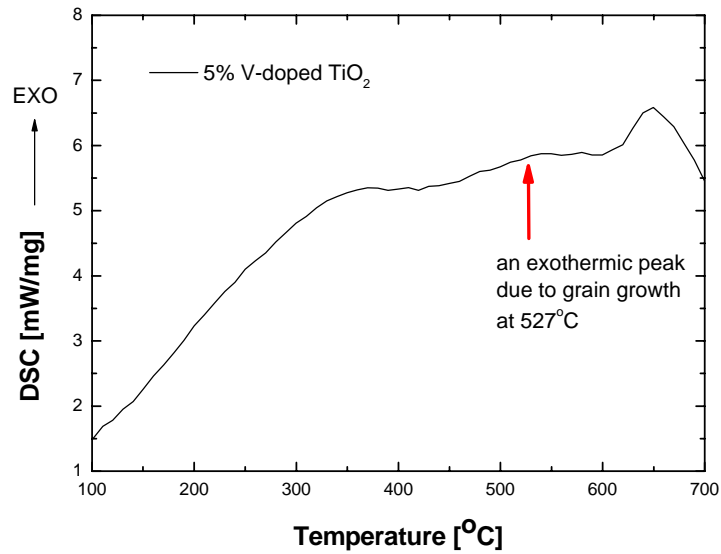


Fig. 3 DSC spectrum of 5%V-doped titania nanopowder.

Based on the Fig. 3, Fig. 4 shows X-ray diffraction patterns of 5%V-doped titania nanopowders heat-treated at 500°C, 600°C, and 700°C in air. Here we could find the behavior of the precipitation, grain growth, and phase transition as mentioned above. Three phenomena occur simultaneously at 600°C. At this temperature, vanadium is precipitated to V₂O₅, anatase is totally changed to rutile, and FWHM of rutile (110) is much sharper, which means the grain growth of rutile particle.

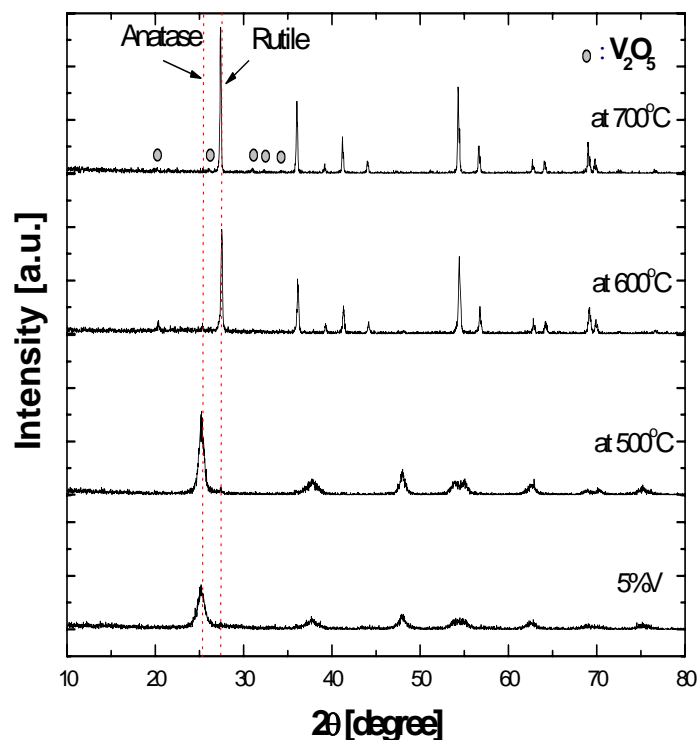


Fig. 4 X-ray diffraction patterns of 5%V-doped titania nanopowders which is heat-treated at various temperatures.

3. Physiochemical characterization of catalysts

Fig. 5 shows the UV-vis absorption spectra of V-doped titania nanopowder with V contents. The absorption behavior is distinguished into two classes. In the low vanadium contents of 0.1~1.0%, the spectra are similar to pure titania but exhibits a little red shift with increasing V contents. In the vanadium contents over 5%, a remarkable absorption in the visible range was observed with a red shift. The notable visible absorption means that the indirect bandgap energy of titania may be changed by doping V and an 3d electron of V^{4+} in valance band is excited into the titania conduction band [8,9]⁸⁹.

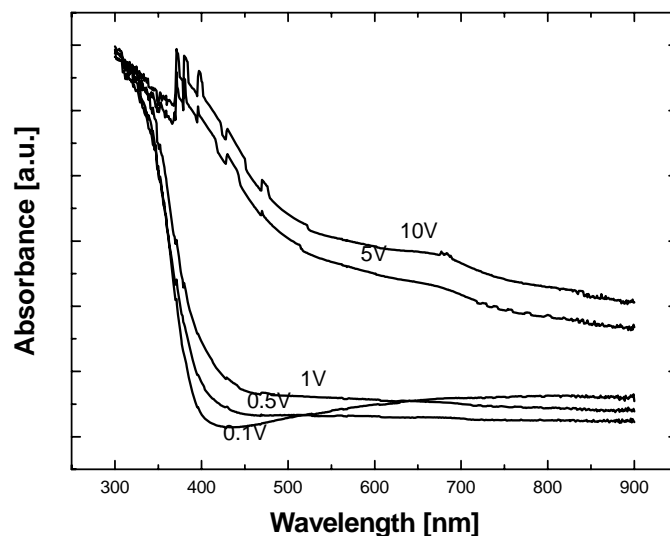


Fig. 5. UV-vis absorption spectra of V-doped titania nanopowders.

Fig. 6(a) shows the FTIR spectra of V-doped titania nanopowders. The absorption intensity related to vanadium oxide is not observed in FTIR spectra and in particular, all the FTIR spectra of titania nanopowder synthesized by AACVS are simpler than that of titania manufactured by other method, having various stretching vibrations due to C-H bonds of organic compound. It is attributed to the high reacting temperature of 1250 °C, at which the V-doped titania by AACVS method is synthesized. At the wavenumber of about 951 cm^{-1} , we can find the effect of V addition into titania. As increasing the V content, the absorption band at 951 cm^{-1} becomes more clearly at samples containing vanadium over 5%. However, the absorption peak is not reported in V-doped titania nanopowder yet.

From the FTIR spectra of heat-treated 5%V-doped titania in Fig. 6(b), two kinds of absorption bands and a transition band could be observed by changing heat-treating temperature to 600°C. The absorption band at 951 cm^{-1} shifts toward a transient absorption band at 982 cm^{-1} after heat treated at 500°C and then disappears after heat treating at 600°C. The vanished band takes place

again at the absorption band of 1025 cm^{-1} , which is known as a typical absorption band of V_2O_5 . It means that V_2O_5 was formed by heat treatment.

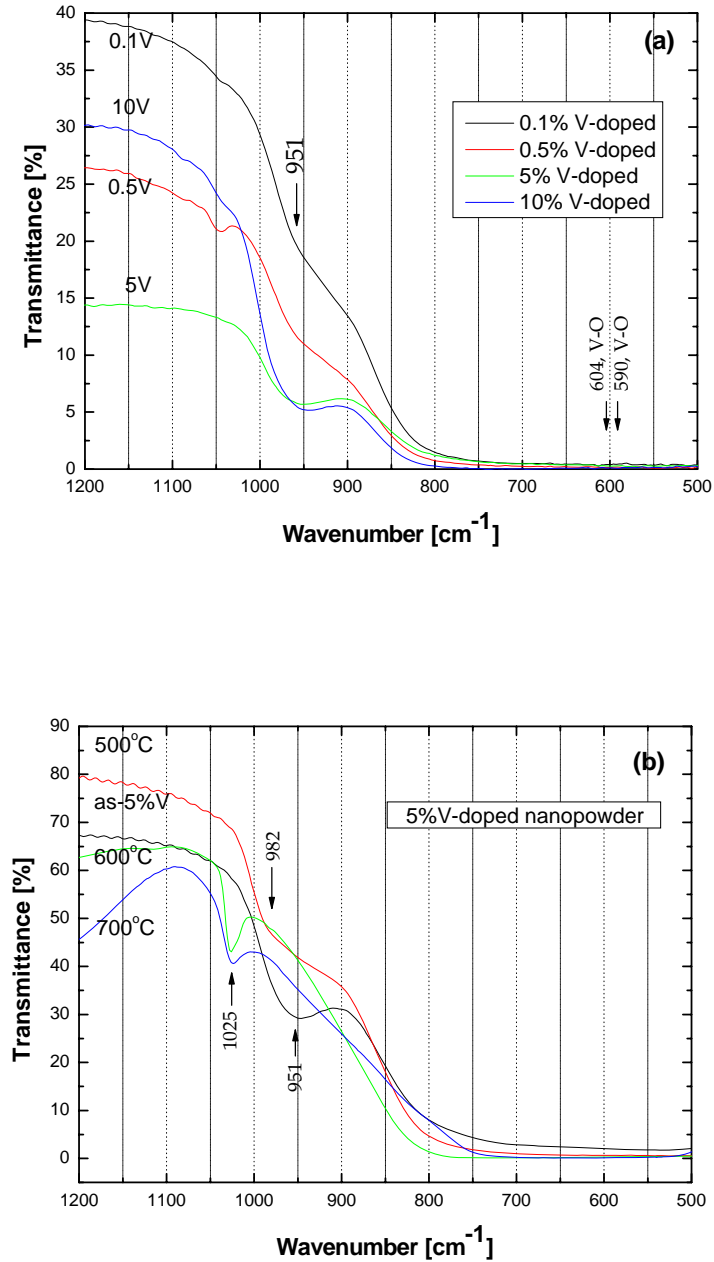


Fig. 6. FTIR spectra of V-doped titania nanopowders (a) and 5%V-doped nanopowders heat-treated at 500, 600, and 700°C.

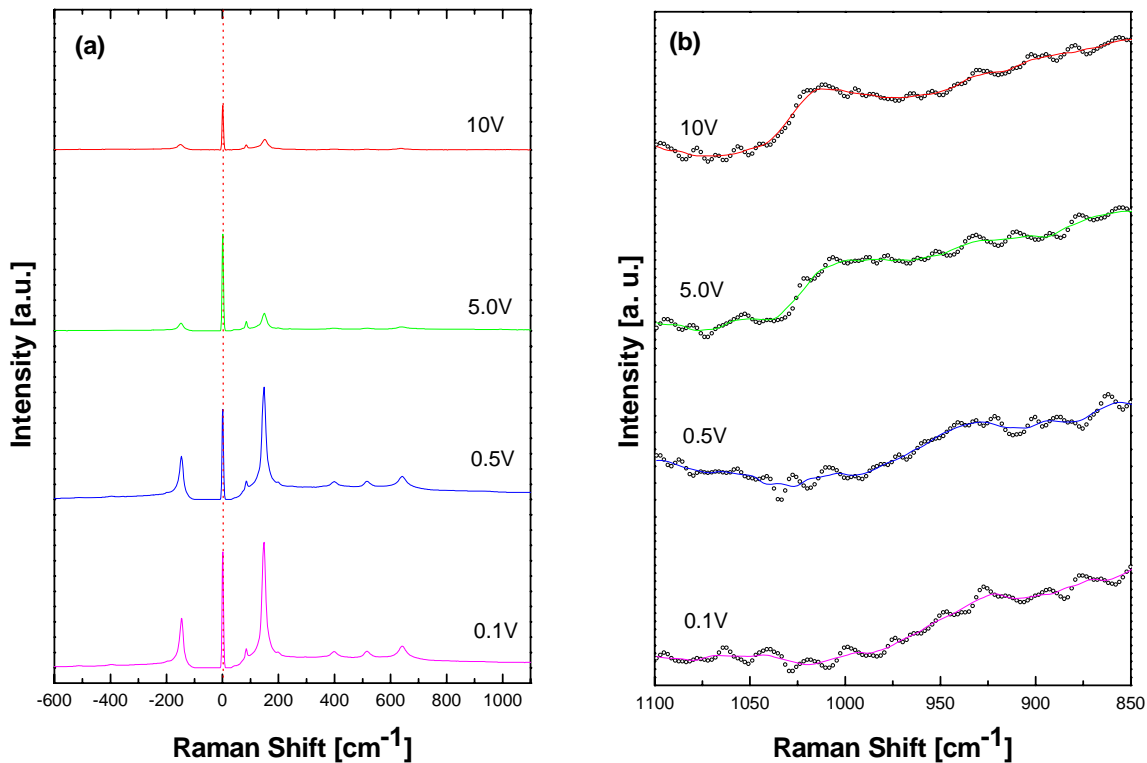


Fig. 7. Raman spectra of V-doped titania nanopowder in a full range of Raman shift (a) and in a local range showing vanadia spectrum (b).

The Raman spectra of V-doped titania nanopowder are presented in Fig. 7 as a function of the contents of vanadium. In Fig. 7(a), the typical spectra of anatase TiO_2 are observed, while there are no vanadia. The intensity of titania spectra are dramatically reduced as increasing the content of vanadium from 0.5% to 5.0%. It is attributed to the low crystallinity of V-doped titania nanopowder due to the lattice distortion developed by the formation of solid solution between titania and vanadia (see the XRD result in Fig 1). On the other hand, Fig. 7(b) shows the existence of vanadia with a very low content, which two kinds of absorption peaks, at 940 cm^{-1} for 0.1%V

and 0.5%V, and around 1020 cm^{-1} for 5.0%V and 10%V, are shown. In Fig. 7(a), however, the vanadium contents are negligible because the vanadia intensity in the local range of 850 cm^{-1} ~ 1100 cm^{-1} is very small.

Discussion

It was reported that the vanadia (vanadium oxide) with bridging V-O-V bond (about 810 cm^{-1} ~ 830 cm^{-1} and 900 cm^{-1} ~ 940 cm^{-1})[10-13]¹⁰¹¹¹²¹³ and terminal V=O bond (about 995 cm^{-1} ~ 1028 cm^{-1})[12-14]¹⁴ is formed in the V-doped titania nanopowder synthesized by wet processes. The vanadium oxide is known to be V_2O_5 but it is not detectable by XRD measurement because its crystallite is too small. Because there is no any peak related to vanadium oxide in Fig. 4 with XRD results in Fig. 1, it can be suggested that V-doped titania synthesized by AACVS formed a fully solid solution without tiny crystallites of vanadium oxide.

As shown in Fig. 4, a new absorption band at 951 cm^{-1} appeared as a function of vanadium contents and disappeared when heating up the titania nanopowder over 600°C, at which V_2O_5 was precipitated. So far, the new absorption band by FTIR measurement is not reported. Since our samples have much simpler FTIR spectra than titania reported in other references [15,16]¹⁵¹⁶, the effect of vanadium dopant on light absorption could be investigated more clearly in this work. Even though we can not explain fundamentally the absorption band, our results above indicate that a vanadium dopant substitutes a titanium cation and formed Ti-O-V bond. In Fig. 7, the V-doped titania nanopowder synthesized at high temperature by AACVS shows the strong Raman spectra of anatase titania and remarkably weak Raman spectra of vanadia. And the Raman spectra of titania were suddenly reduced by the addition of vanadium over 5%.

The results above indicate that the V-doped titania nanopowders synthesized in this study have low bridging V-O-V bonds and lots of bridging Ti-O-V bond due to the formation of many Ti-O-V bond with the fully solid solution of $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ in V-doped titania nanopowder. Consequently it is estimated that the big visible absorption in UV-vis spectra as shown in the Fig. 3 was attributed to the formation of bridging Ti-O-V bond which gives unique photo properties.

Conclusions

In this work, we manufactured V-doped titania nanopowder with vanadium up to 10 atomic percent by AACVS. The titania nanopowders were about 7 nm in average diameter, 200~240 m²/g of specific surface area, and round in shape. Though vanadia was not detectable by XRD and TEM measurements even in 10%V doping contents, EDX, ICP, and XPS revealed that the atomic ratio of the V-doped titania nanopowder is corresponding to the compositional ratio of precursor mixture. With increasing the vanadium contents, the titania nanopowder was scarcely changed in size but the lattice distortion was involved in titania particle. The V-doped titania nanopowder formed Ti_{1-x}V_xO₂ with a fully solid solution. When heat-treated over 600°C, a phase transition from anatase to rutile occurred and a vanadium oxide, V₂O₅, also was separated and precipitated from the V-doped titania nanopowder.

FTIR and Raman measurements revealed that the V-doped titania nanopowders had much more bridging Ti-O-V bond than V-O-V bond. Accordingly, the titania nanopowder showed the red shift behavior as well as a large visible absorption in UV-vis spectra due to the formation of many bridging Ti-O-V bonds with the fully solid solution of Ti_{1-x}V_xO₂. However, the heat-treated V-doped titania nanopowder showed neither the red shift nor the large absorption of visible light.

References

-
- [1] Fujishima, A. and Honda, K. (1972) *Nature*, 238, 37.
 - [2] Zhao, G., Kozuka, H., Lin, H., Takahashi, M., and Yoko, T. (1999) *Thin Solid Films* 340, 125-131.
 - [3] Anpo, M., Takeuchi, Ikeue, K., and Dohshi, S. (2002) *Solid State and Materials Science* 6, 381-388.
 - [4] Stark, W.J., Wegner, K., Pratsines, S.E., and Baiker, A. (2001) *Catalysts* 197, 182-191.
 - [5] Shannon, R.D., (1976) *Acta Crystallogr.* A32, 751.
 - [6] Eror, N.G., J. (1981) *Solid State Chem.* 38, 281.
 - [7] Valigi, Corfisch, M., D., Minelli, G., Natale, P., and Prota, P. (1988) *J. Solid State Chem.* 77, 255.

-
- [8] Mizushima, K., Tanaka, M., Asai, A., and Iida, S. J. (1979) *Phys. Chem. Solids.* 40, 1129.
- [9] Klosek, S., and Raftery, D. (2001) *J. Phys. Chem.* B105, 2815-2819.
- [10] Reddy, E.P. and Rajender, S.V. (2004) *J. of Catalysis* 221, 93-101.
- [11] Sohn, J.R., Cho, S.G., Young, I.P, and Hayashi, S. (1996) *J. of catalysis* 159, 170-177.
- [12] Topsoe, N.Y., Anstrom, M., and Dumesic, J.A. (2001) *Catalysis Lett.* 76, 1-2.
- [13] Kryukova, G.N., Zenkovets, G.A., Mestl, G., and Schlogl, R. (2003) *React. Kinet. Catal. Lett.* 80, 161-169.
- [14] Grahnan, J.L., Almquist, C.B., Kumar, S., and Sidhu, S. (2003) *Catalysis Today* 88, 73-82.
- [15] Nyquist, R.A., and Kagel R.O. (1997) *Infrared and Raman Spectra of Inorganic Compounds and Organic Salts* 4, 214-215 Academic Press.
- [16] Ivanova, T., Harizanova, A., and Surtchev, M. (2002) *Mater. Let.* 55, 327-333.