NEXAFS study of the annealing effect on electronic structure of TiO$_2$ nanoparticles prepared by the sol-gel method

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1. Introduction
Titanium oxide (TiO$_2$) is famous as a photocatalyst. In recent years, it has been applied to perovskite solar cells and organic thin film solar cells in order to achieve high energy conversion efficiency. [1] It is necessary to use TiO$_2$ nanoparticles in order to obtain the smooth interface required to achieve high energy conversion efficiency. Further, by using a solution process such as the sol-gel method, TiO$_2$ nanoparticles can be easily synthesized at low cost. On the other hand, the volume ratio of the surface area to bulk one increases due to the formation of nanoparticles. Therefore, the influence on the surface electronic structure derived from the oxygen deficiency, which is important surface phenomena for the transition metal oxide, becomes large. It is expected that surface-derived structures such as oxygen deficiency in transition metal oxides are strongly related to the conditions of annealing after film formation. We investigate the effect of annealing condition on the surface electronic structure of a thin film of TiO$_2$ nanoparticles by using NEXAFS spectroscopy.

2. Experiment
TiO$_2$ nanoparticles were prepared by the sol-gel method using titanium tetraisopropoxide as a precursor. [2] Specifically, after dissolving the titanium tetraisopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$) precursor in ethanol, it is added dropwise to HCl diluted with stirred ethanol at 0℃, and the mixed solution is added to 5. After stirring for a while, it was diluted 10-fold with ethanol to obtain a TiO$_2$ sol. Further, it was heated at 160℃ for 16 hours in an autoclave. The film was formed by spin coating at 5000 rpm three times for 30 seconds. The annealing was carried out at 500℃ for 30 minutes in an air atmosphere.
and a hydrogen atmosphere, respectively. And also the annealing in an argon was performed at 350°C for 30 minutes. The soft X-ray absorption microstructure (NEXAFS) near the absorption edge is measured at BL-11A of the Photon Factory, using the total electron yield method (TEY) and the fluorescence yield method (FY). For the samples annealed in a hydrogen atmosphere, measurements were performed by the TEY method at BL-7A of the Photon Factory.

3. Results and Discussion

Figure 1 shows a TEM image of the non-annealed TiO₂ nanoparticles. We found that the particle size of the TiO₂ nanoparticles is about 5 to 10 nm.

Figure 1: TEM image of TiO₂ nanoparticles

In Figure 2, we compare the XRD pattern of the purchased anatase-type TiO₂ powder and the TiO₂ nanoparticles prepared by sol-gel method. The XRD diffraction pattern of the purchased anatase-type TiO₂ powder is in good agreement with that of the TiO₂ nanoparticles prepared by sol-gel method. It is confirmed that the TiO₂ nanoparticles prepared by sol-gel method show anatase-type crystal structure.

In Ti L-edge NEXAFS of TiO₂ nanoparticles annealed in the air and argon atmosphere, as shown in Fig.3 (a), and (b), we found that (1) there was no significant difference between the NEXAFS using TEY method and those by FY method. In O K-edge NEXAFS of TiO₂ nanoparticles annealed in the air and argon atmosphere, as shown in Fig.3 (c), and (d), the intensities of the peak at about $h\nu = 531$ eV show a large difference between the NEXAFS using TEY method and those by FY method. They indicates that the oxygen-derived conduction band changes by annealing atmosphere. Furthermore, by considering the detection depth of the TEY and the FY method, this change of the conduction band structure is considered to be due to structural changes related to O atoms such as oxygen deficiency and formation of hydroxyl groups near the surface of the nanoparticles.
References

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Figure 3: NEAXFS of TiO2 nanoparticles at Ti L-edge using TEY (a) FY (b) and O K-edge using TEY (c) FY (d)