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XANES Analysis of Layered Titanate Nanosheets with lamellar mesostructure

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1 Introduction

Two-dimensional metal oxide nanosheets have attracted much attention because of their unique physical and chemical properties. We have developed layered titanate nanosheets with lamellar mesostructure using the lamellar phase of 1,12-dodecanediamine (DDA) self-assembly as a template and these nanosheets were applied to visible light photocatalysts [1]. However, it is difficult to investigate their structure because of the two dimensional nanostructure. Some research groups have reported the effective structural analysis using XAFS spectra toward the TiO_2-derived nanostructures [2]. In this study, XANES measurements were performed to investigate the local structure of layered titanate nanosheets with lamellar mesostructure.

2 Experiment

The synthesis process of layered titanate nanosheets have been reported in literature [1]. Tetraisopropyl orthotitanate (TIPT) was mixed with triethanolamine (TEOA) to form a Ti(IV) compound. A DDA aqueous solution was added to the Ti(IV) stock solution and aged at 373 K for 24 h and kept at 413 K for 96 h. The obtained products were washed with distilled water and ethanol and then dried at 333 K in air. The obtained sample was denoted Ti+DDA+TEOA. TIPT mixed with DDA or TEOA were synthesized to examine the role of DDA or TEOA molecules for the nanosheets formation and they were denoted Ti+DDA and Ti+TEOA, respectively. X-ray absorption spectra were measured at the Photon Factory for High Energy Accelerator Research Organization. Ti K-edge XANES measurements were performed at the beam line BL-7C equipped with Si(111) in a transmission mode at room temperature.

3 Results and Discussion

Layered titanate nanosheets with a lamellar mesostructure were obtained for the synthesis condition of Ti+DDA+TEOA. The XANES spectra of the obtained samples, anatase-type TiO_2 and Na_2TiO_3 are compared as shown in Fig.1. All the spectra exhibit a pre-edge feature consisting of multiple peaks (4964-4974 eV) (Fig.1b), which was followed by white line peaks (4983-5003 eV) (inset in Fig.1a). The pre-edge multiple peaks can be assigned to forbidden transitions from the core 1s level to unoccupied 3d state of a Ti(IV). According to the position of edge energy and the presence of pre-edge, it was considered that Ti ions in the layered nanosheets were mainly present as Ti(IV). In the pre-edge of the Ti K XANES for Ti+DDA+TEOA and Ti+DDA, relative intensity of peak B was higher compared with anatase and Ti+TEOA, and the peak feature was similar to titanate such as $Na_2Ti_3O_7$. However, the intensity profiles of peak C were notably different for Ti+DDA+TEOA and $Na_2Ti_3O_7$ (Fig.1b). The white line region in the XANES features arises from dipole-allowed transitions from the core 1s to unoccupied 4p states (inset in Fig.1a). Two excitation peaks (E and F) were observed for $Na_2Ti_3O_7$. In contrast, the peak feature of Ti+DDA+TEOA was different from that of $Na_2Ti_3O_7$ and was very similar to that of lepidocrocite shown in the previous paper [2]. Thus, XAFS spectra imply that the local structure of Ti+DDA+TEOA might be closer to that of lepidocrocite titanate than $Na_2Ti_3O_7$.

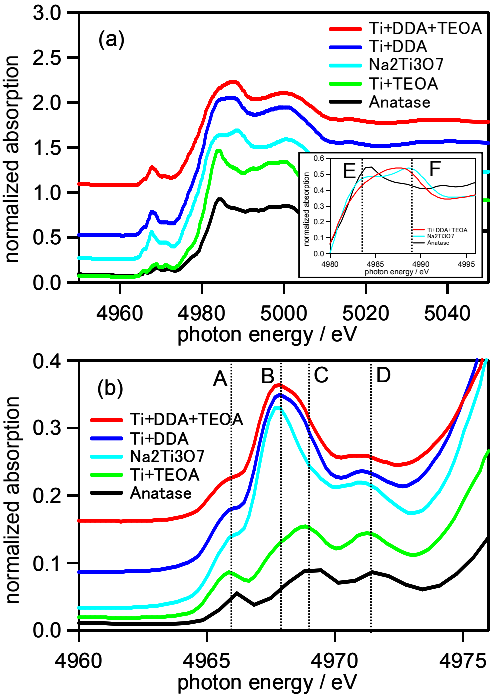

Fig. 1. (a) Ti K edge XANES spectra, inset: enlarged white line regions, (b) enlarged pre-edge regions of layered titanate nanosheets in comparison with other samples.

References

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