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A Comparative XANES Study for Layered Titanate Nanosheets With and Without Lamellar Mesostructure

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1 Introduction

Two-dimensional metal oxide nanosheets are attractive nanomaterials because of their unique physical and chemical properties. We have developed layered titanate nanosheets using lamellar self-assemblies as templates [1]. The effects of amine surfactants on the formation and photocatalytic activities have been studied; however, it was difficult to investigate the local structure of layered titanate nanosheets because of the two dimensional nanostructure and little attention has been given to the effects of a lamellar mesostructure. In this study, XANES measurements were performed to investigate the local structure of layered titanate nanosheets with and without 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. The pH was adjusted from 8.0 to 12.8 by adding aqueous HCl or NH_4OH as necessary. The mixture was 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 is denoted Ti+DDA+TEOA. The pH for each synthesis is given in parentheses. 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

A lamellar mesostructure was observed for Ti+DDA+TEOA prepared at pH ranging from 10.0 to 11.0. Thus cconsiderable differences were found in the mesostructure of layered titanate nanosheets fabricated at different pH. The XANES spectra of Ti+DDA+TEOA (10.5) with lamellar mesostructure, Ti+DDA+TEOA (12.8) without lamellar mesostructure and anatase TiO_2 are compared in Figure 1. All the spectra exhibit a pre-edge feature consisting of multiple peaks (4964–4974 eV), which was followed by white line peaks (4983–5003 eV). The pre-edge multiple peaks can be assigned to forbidden transitions from the core 1s level to unoccupied 3d state of Ti^{IV} [2]. According to the position of the edge energy and the presence of a 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 (10.5) and Ti+DDA+TEOA (12.8), the relative intensity of peak C was higher compared with that of anatase and the peak feature of the layered titanate nanosheets differed from that of anatase. The white line region in the XANES features arises from dipole-allowed transitions from the core 1s to unoccupied 4p states [2]. Excitation peak A (inset of Figure 1(a)) was similar in both layered titanate nanosheets and the peak might be close to that of lepidocrocite titanate [2]. X-ray absorption fine structure spectra imply that there is little difference between the local structure of Ti+DDA+TEOA (10.5) and Ti+DDA+TEOA (12.8).

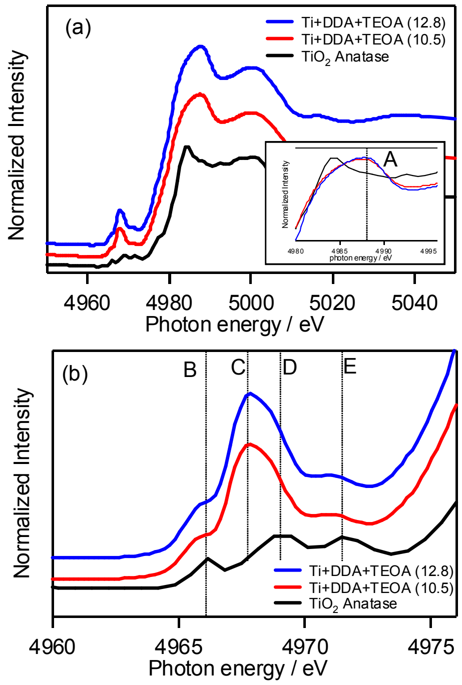

Fig. 1. (a) Ti K edge XANES spectra and (b) enlarged pre-edge regions of Ti+DDA+TEOA (10.5) and Ti+DDA+TEOA (12.8) with that of anatase TiO_2 for comparison. The inset in (a) shows an enlargement of white line regions.

References

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