

Electronic Structure of Anatase (TiO₂) by means of X-ray Raman Scattering.

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1 Introduction

Titanium dioxide (TiO₂) occurs in nature as three different polymorphs. Other than most common rutile structure, it forms anatase and brookite structures. Among them, anatase shows strong photocatalytic activity. Though the anatase has been studied extensively, the electronic properties are not made clear enough, because TiO₂ is an insulator and thus photoemission, most general method, cannot be applied basically.

We have reported X-ray emission spectra (XES) of some Ti-compounds, which include X-ray Raman scattering (XRS) and fluorescence.[1] The XRS spectra, excited by the photon energy just below the absorption edge, can observe electronic structures of unoccupied state of materials, regardless of its conductivity. In the case of TiO₂, Ti 3*d* state can be observed clearly.

2 Experiment

The XRS and Ti *K* XAS experiments were performed at beamlines BL7C and BL15B1. X-ray emission spectra having an energy centered at the Ti *Kα* fluorescence lines (*Kα*₁=4510.84 and *Kα*₂=4504.86 eV) were observed. The spectrum changes continuously from *Kα* fluorescence to XRS when the excitation energies are changed from above to below the absorption edge. The fluorescence peaks have constant emission energies, while each XRS peak has each constant loss-energy from the excitation energy (Raman shift). The energy resolution for both the Ti *K* XAS and XRS measurements was about 1 eV for 5 keV photon.

Commercially obtained powder sample (Furuuchi Chemical Co.) and epitaxially grown single crystal were used in this experiment. The single-crystal anatase TiO₂(001) thin films were grown using PLD on LaAlO₃(100) and has 500 nm thickness.[2] The crystallinity of the sample was checked by XRD measurement.

3 Results and Discussion

Figure 1 shows XRS spectra of rutile and anatase, excited by same energy (4964.9 eV). Though only the spectra of powder samples are shown in the figure, single crystal anatase showed similar spectrum. Both of the XRS spectra show seven peaks which are originated from excitation including pairs of Ti 2*p* core-hole and excited electron in unoccupied state. The three peaks at high

energy correspond to the electrons in Ti 4*p* state, while the four peaks at low energy correspond to those in Ti 3*d* state. The Ti 3*d* peaks consist of two pairs, because of the spin-orbit interaction of Ti 2*p* state (*L*_{III} and *L*_{II}), and each pair is split into *t*_{2*g*} and *e*_g by ligand field (in *O_h* approximation).

As can be seen in the figure, the *e*_g peaks in anatase are weaker than that of rutile, suggesting that the *e*_g state in anatase is more occupied. Since the *e*_g orbital is oriented to O-ions and is hybridized with O 2*p* state, the result means that the hybridized Ti 3*d* electrons in anatase are more localized. On the other hand, the lowest energy peak of Ti 4*p* spectrum of anatase shows lower intensity. Since the peak corresponds to Ti 4*p*_L state in XAFS spectrum, where _L denote ligand hole, dynamical charge transfer from ligand oxygen to titanium is weak in anatase. This result is consistent with the localization of Ti 3*d* electron in ground state. Such localization of 3*d* electrons would result high efficient photo-excitation on Ti site under UV irradiation; i.e. high efficient photocatalyst.

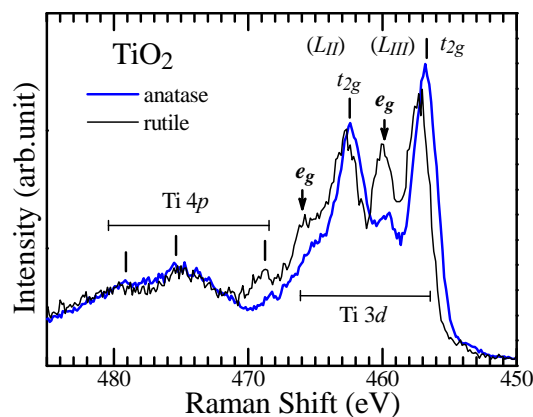


Fig. 1: XRS spectra of TiO₂. Comparison between the spectra of rutile and anatase.

References

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