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First-principles study of photocatalytic activity of amorphous TiO_2 surface

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Abstract

To clarify amorphous surface structures on anatase TiO_2 that contribute to improve the catalytic activity, we generated amorphous surface models of TiO_2 and performed first-principles PAW calculations of Ti *L*-edge ELNES (Electron energy-loss near-edge structures) spectra. Simulated *L*-edge ELNES of 4-coordinated Ti (^{4c}Ti) in amorphous TiO_2 were in good agreement with the spectra of the surface region reported to have good photocatalytic activity in the experiment. We also performed adsorption simulations of water molecules on the amorphous surface. We found that charged defects near surface affect adsorption energies.

1. Introduction

Photocatalysts have attracted much attention for their deodorant, antifouling, antibacterial, and hydrophilic effects, and are active in various fields such as medical care, agriculture, and construction. Among them, TiO_2 is a typical photocatalytic material that is relatively inexpensive and highly safe, and has been actively studied to improve its performance for wider range of applications. One of our group reported that the formation of an amorphous structure on TiO_2 surface improved the catalytic activity, and that it was reduced when the amorphous surface was scraped by etching. Therefore, it is considered that the control of the amorphous surface is the key of improving the catalytic activity.

STEM-EELS has been widely used in recent years to observe nanoscale atomic and electronic structures with high spatial resolution. In particular, ELNES is able to provide sensitive information on chemical bonding, valence states and coordination. We observed amorphous surfaces of TiO_2 samples with high photocatalytic activity using the atomic-resolution electron microscope (JEOL ARM-200F @NITech), and found that spectra of the surface region were significantly different from those of bulk region. However, the atomic structure has not yet been identified. In this study, we identify amorphous surface structures that contribute to improve the catalytic activity using first-principles calculations, combining with electron-microscopy observations. Furthermore, we investigate the origin of its high catalytic activity via adsorption simulations.

2. Computational method

Amorphous surface models for anatase TiO_2 were generated by quenching from the melt using classical MD method and subsequent relaxation using first-principles method with VASP code [1]. Structural relaxation with VASP code did not significantly change the basic continuous bonding network. Ti *L*-edge ELNES were simulated for those models with QMAS code [2], including of the core-hole effects. We employ the projector augmented-wave (PAW) method with GGA-PBE+U functional for these electronic state calculations.

3. Results and discussion

Fig. 1 shows one of amorphous surface models. The coordination number of Ti with oxygens is six in the bulk region, while that is four in the amorphous surface region. Fig. 2 shows calculated Ti *L*-edge ELNES spectra of the surface and bulk region in an amorphous surface model, in comparison with experimental ones of the TiO_2 thin film with good catalytic activity. The calculated spectra are shifted to higher energy by 1.5 eV to match the first peak of the L_3-edge of the experimental one. For both experimental and calculated spectra, the 4-coordinated Ti (^{4c}Ti) has less spectral splitting than the 6-coordinated Ti (^{6c}Ti), and the peak of ^{4c}Ti is located at slightly higher energy side. These spectral differences between ^{6c}Ti and ^{4c}Ti can be explained based on the crystal field theory. We can conclude that the coordination number of Ti in amorphous surface region of TiO_2 thin film should be four.

Our photoluminescence experiments suggest that surface defects are present in TiO_2 thin films. It was found that eigen levels of oxygen-deficient defects appear at the almost same energy in the band gap as the experiments, as shown in Fig. 3. We calculated the adsorption energies defined as $E_{ads} = E_{H2O/surface} - E_{H2O} - E_{surface}$. In charge neutrality, the presence of oxygen-deficient defects did not affect E_{ads}. However, in the positively charged state, E_{ads} for the model with defects is 0.18 eV lower than that without defects. This indicates that positively charged defects near surface enhance hydrophilicity.

4. Conclusions

To clarify amorphous surface structures on anatase TiO_2 that contribute to improve the catalytic activity, we generated amorphous surface models of TiO_2 and performed first-principles PAW calculations of Ti *L*-edge ELNES (Electron energy-loss near-edge structures) spectra. Simulated *L*-edge ELNES of 4-coordinated Ti in amorphous TiO_2 were in good agreement with the spectra of the surface region reported to have good photocatalytic activity in the experiment. We found that charged defects near surface affect adsorption energies. It can be thought that oxygen-deficient defects in the ^{4c}Ti amorphous surface are the key to further enhancing catalytic activity.

References

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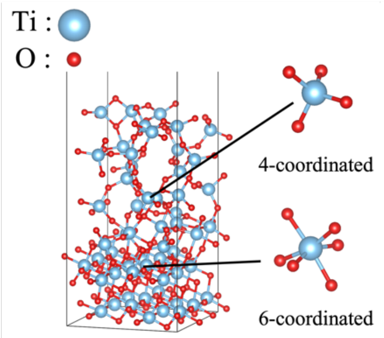

Fig. 1 Amorphous surface model on anatase TiO_2.

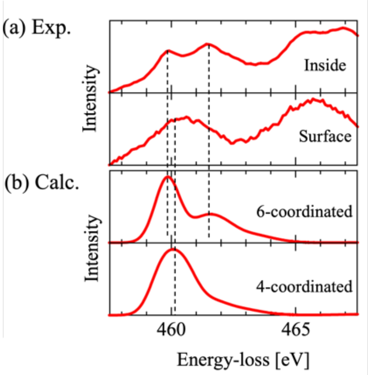

Fig. 2 Experimental and calculated Ti L_{23}-edge spectra.

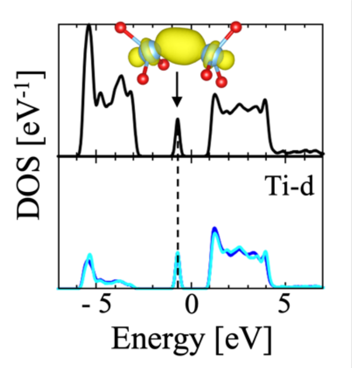

Fig. 3 DOS of oxygen-deficient defects near 4-coordinated Ti.
The arrow indicates the defect state.
The electron-density isosurface for the defect state is also shown.