

Heterometallic Frameworks Thin-film measured by a compact Low-Temperature Polarization-dependent Total Reflection Fluorescence XAFS

Wang-Jae CHUN*

¹ College of Liberal Arts, Division of Arts and Sciences, International Christian University,
3-10-2 Osawa, Mitaka, Tokyo, 181-8585, Japan

1 Introduction

Metal-organic frameworks (MOFs) are among the most active areas in materials research due to facile structural architectures and potentially interesting properties in numerous applications, including hydrogen storage, absorbents, and catalysts. Among these applications, intensive studies in fabricating growth orientation-controlled MOF thin films without losing bulk phase properties for sensor devices. Another trend is introducing multiple metal components to build highly functional MOFs thin films. Because most MOFs are homometallic, containing only one kind of metal in the framework. Understanding the coordination geometry of the multi-metal centers on substrates is crucial to achieving the goal. Chun et al. have developed a compact low-temperature Polarization-dependent Total Reflection Fluorescence XAFS (PTRF-XAFS) for unraveling the problems.

This report will show that the LT-PTRF-XAFS can contribute to enlightening the coordination geometry of multi-metal centers in heterometallic Frameworks thin films.

2 Experiment

XAFS measurements were performed at the BL-12C of KEK-PF-IMSS (2.5 GeV, 450 mA, Si(111)) with the compact LT-PTRF-XAFS measurement system^[2] using liquid nitrogen as a cheap cold agent. Mn and Co K α Fluorescence signals were detected with 7-elements Silicon Drift Detector (XSD50-07, Techno AP, Japan).

As a sample, the author employed PPF-3-MnCo^[3] in this work, which allows the three-dimensional (3D) stacking without sacrificing the final topology. PPF-3-MnCo thin films on TiO₂(110) were prepared by the solvothermal method. Demeter and REX2000 were used for XAFS analysis. *PPFs: a porphyrin paddle-wheel framework.

3 Results and Discussion

Fig. 1 shows Mn and Co K-edge EXAFS spectra of PPF-3-MnCo on TiO₂(110) at RT and 80 K with bulk as a reference. Except for the slightly weakened amplitude of films, the $k^2\chi(k)$ EXAFS spectra showed no specific difference between the thin film and bulk as a reference. Moreover, there is no dramatic S/N ratio improvement in the high k -vector region by lowering measurement temperature. Presumably, it assumes that the significant contribution of the spectra will be metal-oxygen interactions which are less sensitive to temperature.

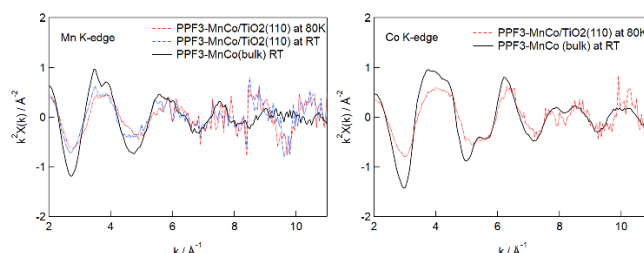


Fig. 1 Mn and Co K-edge $k^2\chi(k)$ EXAFS results of PPF3-MnCo/TiO₂(110) with bulk as a reference.

Fig. 2 shows Mn and Co K-edge XANES spectra of PPF-3-MnCo on TiO₂(110) at RT and 80 K. Firstly, unique pre-edges ($1s \rightarrow 3d$ transition) were found for both Mn and Co K-edge XANES. There was no specific difference in Mn K-edge except for the peak intensity. The intensity of 80 K was stronger than those of RT and bulk.

Unlike Mn K-edge, an energy shift was observed between RT and 80 K in Co K-edge. Moreover, the intensities of thin films were almost identical, but they were stronger than that of bulk. These remarkable results suggest that the coordination geometry of the Co center is more sensitive than that of the Mn center.

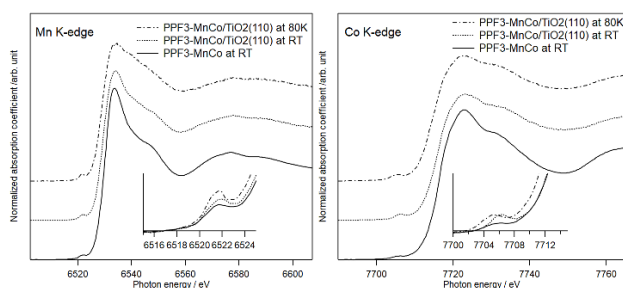


Fig. 2 Mn and Co K-edge XANES results of PPF3-MnCo/TiO₂(110) with bulk as a reference.

Acknowledgment

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References

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* wchun@icu.ac.jp