

Ultra thin Metal-Organic Framework $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n$ film on $\text{TiO}_2(110)$

Miyuki Hashimoto¹, Satoshi Okajima², Toshihiro Kondo¹, Kenji Hara³, and Wang-Jae Chun^{2*}

¹Graduate School of Humanities and Sciences, Ochanomizu University Tokyo 112-8610, Japan

²Graduate School of Arts and Sciences, International Christian University, Tokyo 181-8585, Japan

³Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

1 Introduction

Metal-organic frameworks (MOFs), hybrid inorganic-organic solid compounds with high designability of geometry, size, and functionality, are widely regarded as promising materials for catalysts, separation, gas storage, and molecular recognition.[1-2]

For understanding the growth mechanism of MOF film, XRD is the most common method, but it requires thick films generally. Even synchrotron radiation XRD has difficulties to obtain distinguishable signal from less than 10 multi-layered films. Overcoming this challenge, XAFS, will be an alternative probe. Especially, it has been demonstrated that polarization-dependent total reflection fluorescence XAFS (PTRF-XAFS) technique is a powerful tool for obtaining 3D structure on a flat substrate.[3]

In this study we have examined the structure of HKUST-1¹² ($[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n$; BTC = 1,3,5-benzenetricarboxylate) ultra thin films on a single crystal $\text{TiO}_2(110)$ surface by PTRF-XAFS. HKUST-1 is one of well-known functional MOFs.[4]

2 Experiment

A $\text{TiO}_2(110)$ was initially immersed in a saturated BTC ethanol solution at 348 K for 24 hours. The substrate was then alternatively immersed in $\text{Cu}(\text{OAc})_2$ ethanol solution (1 mM) for 30 minutes and in BTC ethanol solution (1 mM) for 1 hour at r.t. The coverage of 1 cycle thin film was 1.45×10^{13} HKUST-1 molecules/cm², which was determined from $\text{Cu}_{2p_{3/2}}$ to $\text{Ti}_{2p_{3/2}}$ peak area ratios by XPS (Al K α , Thermo K-Alpha).

PTRF-XAFS were performed at the BL12C of Photon Factory (2.5 GeV, 450 mA, Si(111); PAC No. 2012G071) in fluorescence mode. Considering the anisotropic surface structure of $\text{TiO}_2(110)$, XAFS were carried out in three different orientations relative to the electric vector (\mathbf{E}) of the incident X-rays.[3] Data analysis was processed using REX 2000 (Rigaku) and FEFF code.

3 Results and Discussion

The XANES spectrum of bulk HKUST-1 has characteristic features denoted as (I), (II), and (III) as shown in Fig. 1(A). Prestipino *et al.* have reported that the peaks at *ca.* 8998 eV and at *ca.* 8977 eV ascribed to the quadrupolar transition $1s \rightarrow 3d$ and the white line, respectively.[5] They also assigned that the peak at *ca.* 8985 eV is due to the $1s \rightarrow 4p$ dipolar shakedown transition. We found these peaks in the ultra thin film,

indicating that HKUST-1 cage structure was formed on the $\text{TiO}_2(110)$ surface even at the 1 cycle process.

Similarly to the XANES spectra, all EXAFS spectra of the film were relatively identical to that of a bulk HKUST-1, especially in 3.7 to 7.0 \AA^{-1} range (Fig. 1(B)). As be different with two in-plane orientations, the amplitude of out-of-plane ($\mathbf{E} // [110]$) orientation was slightly dampened, but not significantly. Curve fitting results suggest that the main contribution was both $\text{Cu}_{\text{abs}}\text{-O}$ and $\text{Cu}_{\text{abs}}\text{-Cu}$ interactions. We could not get meaningful fitting parameters for out-of-plane when $\text{Cu}_{\text{abs}}\text{-Ti}$ was included. The bond distances of $\text{Cu}_{\text{abs}}\text{-O}$ and $\text{Cu}_{\text{abs}}\text{-Cu}$ were estimated at about 1.97 ~ 1.98 \AA and 2.69 ~ 2.72 \AA , respectively. Both the coordination numbers and distances were within their error obtained from the refined single-crystal XRD ($\text{Cu-O} = 1.96 \text{\AA}$; $\text{Cu-Cu} = 2.63 \text{\AA}$).[4] Moreover, there was no significant difference in the coordination numbers. These XAFS results suggested that a HKUST-1 crystallite/nucleus formed in the initial stage of the thin film growth.

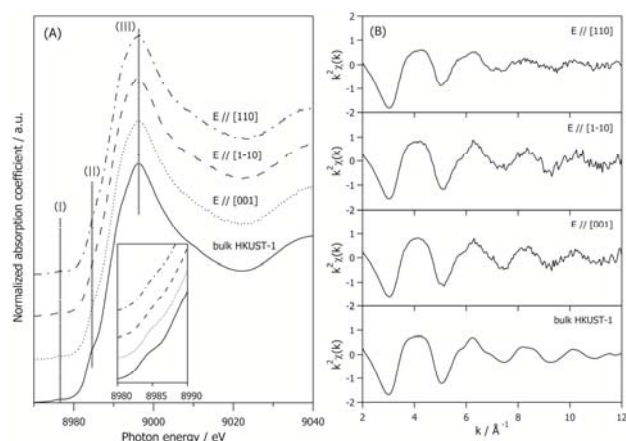


Fig. 1: Cu K-edge PTRF-XAFS spectra of 1 cycle and bulk HKUST-1 in three different polarization directions. (A) Normalized XANES spectra and (B) k^2 -weighted EXAFS oscillations..

References

- [1] S. Kitgawa, *et al.*, *Chem. Lett.*, 623 (1991).
- [2] O. M. Yaghi, *et al.*, *Nature*, **378**, 703 (1995).
- [3] W.-J. Chun, *et al.*, *J. Phys. Chem. B*, **102**, 9006 (1998)
- [4] S. S. Y. Chui, *et al.*, *Science*, **283**, 1148 (1999)
- [5] C. Prestipino, *et al.*, *Chem. Mater.*, **18**, 1337 (2006).

*wchun@icu.ac.jp