Fabrication of highly oriented crystalline pillared-layer-type metal-organic framework thin film by casting method

([1] *Department of Chemistry, Faculty of Science, Tokyo University of Science*)
○QIYUAN ZHANG,[1] TOMOYUKI HARAGUCHI,[1] TAKASHIRO AKITSU[1]

Keywords: surface/interface; metal-organic framework

Metal-organic frameworks (MOFs) are a kind of porous material with adsorption capabilities that are formed from a combination of metal cations and organic linkers. They have attracted attention for fuel storage, carbon dioxide capture, and catalysis[1]. Recently, crystalline-oriented MOF thin films have been intensively pursued, which have been expected for their potential use as gas sensors and proton-conducting membranes[2]. The layer-by-layer method, which involves sequentially soaking substrates in a solution containing the components of the MOF to construct the film structure, has been the typical method for fabricating thin films to date[3]. However, the method is complicated and too costly to construct thin films.

In this study, we aimed to fabricate crystalline-oriented pillared-layer-type MOF thin films using the casting method. $Fe[Pt(CN_4)]$ nanosheets were synthesized and a colloidal solution was cast onto the substrate, which was subsequently dried to form a 2D $Fe(H_2O)_2[Pt(CN)_4]$ thin film (**film-H**). As shown in Figure of X-ray diffraction (XRD) patterns of **film-H**, *hk*0 and 00*l* diffraction peaks are separately observed in the in-plane and out-of-plane patterns, respectively, which indicates that the obtained thin film was highly crystalline, and its orientation was accurately controlled. After dehydration by vacuum heating, **film-D** was obtained, and 3D pillared-layer-type $Fe(pz)[Pt(CN)_4]$ thin film (**film-pz**) was fabricated by casting pyrazine solution onto **film-D**. The XRD measurements also confirmed the high crystallinity and controllable orientation of **film-pz**.

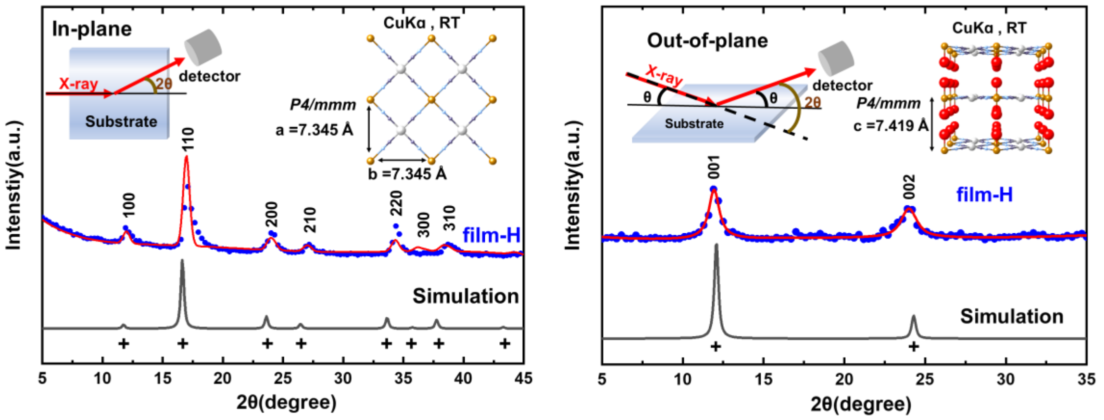

Figure XRD patterns of **film-H** (λ = 1.540 Å, rt). Left: In-plane (grazing-incidence mode) patterns, right: Out-of-plane (θ–2θ mode) patterns.

(1) H. Furukawa *et al*., *Science* **341**, 1230444 (2013). (2) O. Shekhah *et al*., *Chem. Soc. Rev.*, **40**, 1081-1106 (2011). (3) K. Otsubo *et al*., *J. Am. Chem. Soc.*, **134**, 9605-9608 (2012). (4) T. Haraguchi *et al*., *Inorg. Chem.*, **54,** 11593-11595 (2013).