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Negative, anisotropic thermal expansion in monolithic thin films of crystalline metal-organic frameworks

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ABSTRACT

The unusual thermal expansion properties of a prototype nanoporous, crystalline solid have been determined by studying epitaxially grown, highly oriented thin films rigidly anchored to a solid substrate using out-of-plane and in-plane X-ray diffraction (XRD). The analysis of the data for the particular metal-organic frameworks (MOFs) studied here, HKUST-I, reveals a thermal expansion which is negative for the direction perpendicular and positive for the direction parallel to the substrate surface. The corresponding anisotropic coefficients of thermal expansion (CTE) amount to $(-75 \pm 16) \times 10^{-6}\ K^{-1}$ in the direction perpendicular to the substrate and to $(11.7 \pm 3.7) \times 10^{-6}\ K^{-1}$ in the direction parallel to the substrate surface. These values substantially differ from the intrinsic CTE, measured for powder MOFs ($-4.1 \times 10^{-6}\ K^{-1}$). The substrate-induced anisotropic thermal expansion allows for a direct measurement of the Poisson's ratio of MOF materials, which is hardly measurable for powder MOFs. The Poisson's ratio of HKUST-1 was determined to be 0.69 ± 0.37. Furthermore, thermal cycling experiments of the HKUST-1 SURMOFs reveal a pronounced stability, a necessary requirement for using MOFs in thermal response sensor devices and for high-temperature membrane separation.

1. Introduction

Metal-organic frameworks (MOFs) are a rather new class of porous crystalline materials, which have attracted considerable attention from scientists of various fields [1,2]. Although most applications use MOF powders, these porous frameworks are also well suited for the fabrication of homogeneous, dense and highly functional coatings on solid substrates [3–6]. MOF-based coatings possess a great potential with regard to a variety of technological advanced applications such as QCM-based sensors [7–9], membranes for enantiomer separation [10,11], and catalytically active coatings [12]. Furthermore, the possibility of integrating multi-functional MOF thin films into miniaturized optoelectronic, sensor, lab-on-a-chip, or micro-fluidic devices, provides strong stimuli towards technical applications [4]. Using such surface-mounted MOFs, SURMOFs [13], for device application, knowledge about thermal expansion and the strength of the adhesion to the substrate are crucial since the operating conditions often involve substantial variations of temperature.

Most solid materials have a positive coefficient of thermal expansion (CTE), they expand upon heating and contract upon cooling. For MOFs composed of metal nodes connected by organic linkers, a different situation is encountered, here the CTE is negative [14,15]. This phenomenon is related to a temperature-induced excitation of vibrational modes within the organic linkers, resulting in the shrinking of their longitudinal extension and, correspondingly, a contraction of the MOF structure. MOF thin films, and in particular SURMOFs, anchored rigidly to a solid substrate with positive thermal expansion coefficient, will thus experience a pronounced stress upon heating. This stress may induce mechanical failure of the MOF-coatings, for example delamination from the substrate or irreversible structural changes, e.g. internal micro-cracking. To this end, the understanding of thermal expansion relationship between thin MOF films and solid substrates is of great importance for the design of devices where MOF coatings are employed.

In this study we use a particular MOF, HKUST-I, for the fabrication of surface-mounted MOF thin films (SURMOFs). HKUST-I is well suited for a systematic study since in previous work theoretical as well as experimental results for the mechanical properties of this nanoporous, crystalline solid have been reported [16,17]. In

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addition, values for the thermal expansion properties of powder HKUST-1 MOFs are also available from theoretical work [14,16]. HKUST-1 SURMOFs investigated here were grown on a 16-mercaptohexadecanoic acid (MHDA)-functionalized gold substrate by liquid-phase epitaxy (LPE). This method has been described in detail in previous work [18,19]. Among the different methods used for MOF thin film fabrication [20], the LPE method, has the advantage that it yields highly crystalline, homogeneous and oriented MOF thin films. In particular, the high degree of orientation within the monolithic thin films greatly simplifies a quantitative and directional analysis of temperature induced structure changes within the MOFs [5]. HKUST-1 is a molecular framework composed of copper paddle wheel units linked by 1,3,5-benzenetricarboxylate ligands to form a highly symmetric, three-dimensional cubic framework (see the structure in Fig. 1A) [21]. In previous work, it has been shown that powder HKUST-1 MOF crystals exhibited an isotropic negative thermal expansion with a CTE of -4.1×10^{-6} K^{-1} [14]. In the present work, investigations of the thermal response of HKUST-1 SURMOFs in the directions perpendicular and parallel to the substrate surface have been carried out by *in-situ* (i.e. during heating) out-of-plane and in-plane XRD (X-ray diffraction). By tracking the change of the lattice constant induced by the supporting Au@Si substrate, we are able to directly determine the Poisson's ratio of these MOF thin films. Since such measurements have not yet been reported, so far only theoretically calculated Poisson's ratio of MOF crystals were available [22,23]. In an additional setup experiment, the stability of the HKUST-1 SURMOFs under repeated heating-cooling cycles was studied.

2. Experimental section

The basic substrates used in the experiments were Si wafers (commercially available from Wacker Chemie AG), onto which first a 5 nm thick titanium film and then 100 nm of Au were deposited. For supporting and directing the SURMOF synthesis, the gold surfaces were functionalized by 16-mercaptohexadecanoic acid (MHDA, Aldrich) self-assembled monolayers (SAMs). These SAMs expose COOH-terminated organic surfaces [24,25].

The SURMOF samples were prepared in a layer-by-layer fashion using the spray method [19]. The functionalized substrates were, in an alternating fashion, sprayed with a 1 mM solution of $Cu_2(CH_3COO)_4.H_2O$ (Aldrich) in ethanol and 0.1 mM solution of 1,3,5-benzenetricarboxylic acid (BTC, Aldrich) in ethanol. Between each step the substrates were sprayed with ethanol to remove unreacted, weakly adsorbed reactants.

For stability investigations, a fresh HKUST-1 SURMOF was heated in the oven at 100 °C for 30 min and subsequently cooled to room temperature for 30 min. After ten cycles of heating and cooling, the sample was checked by XRD and SEM and compared with an identical reference sample.

The out-of-plane XRD measurements were carried out using a Bruker D8-Advance diffractometer in θ-θ geometry equipped with a PSD Lynxeye®. The in-plane XRD measurements were carried out using Bruker D8 Discover equipped with a quarter Eulerian cradle, tilt-stage and 2.3° Soller-slits were installed in both sides. A Göbel-mirror, a PSD Lynxeye® in θ-2θ geometry and Cu-anodes (Cu $K\alpha_{1,2}$-radiation with $\lambda = 0.15418$ nm) were used in the measurements. The in-plane and out-of-plane measurement were carried out in the range of $2\theta = 5°-20°$ at a scan step of 0.02° at 40 kV and 40 mA.

Scanning electron microscope (SEM) measurements were carried out using a Philips XL SERIES 30 ESEM-FEG. To increase the image contrast and the resolution, the samples were coated with a 5 nm thick gold layer before recording the SEM micrographs.

The *in-situ* heating out-of-plane XRD measurements were performed with a PAAR HTK 1200 heating stage which was installed into the Bruker D8-Advance diffractometer. The heating rate was set to 1 K per minute and the temperature range was set between room temperature and 453 K. The stage temperature was calibrated using Boron Nitride [26].

The *in-situ* heating in-plane XRD measurement were carried out with a special adapted heating stage made by Mesicon (Dr. Ecker scientific consulting, Germany).

3. Results and discussion

The out-of-plane and in-plane X-ray diffractograms (Fig. 1B) confirm that the HKUST-1 thin films are highly crystalline and are

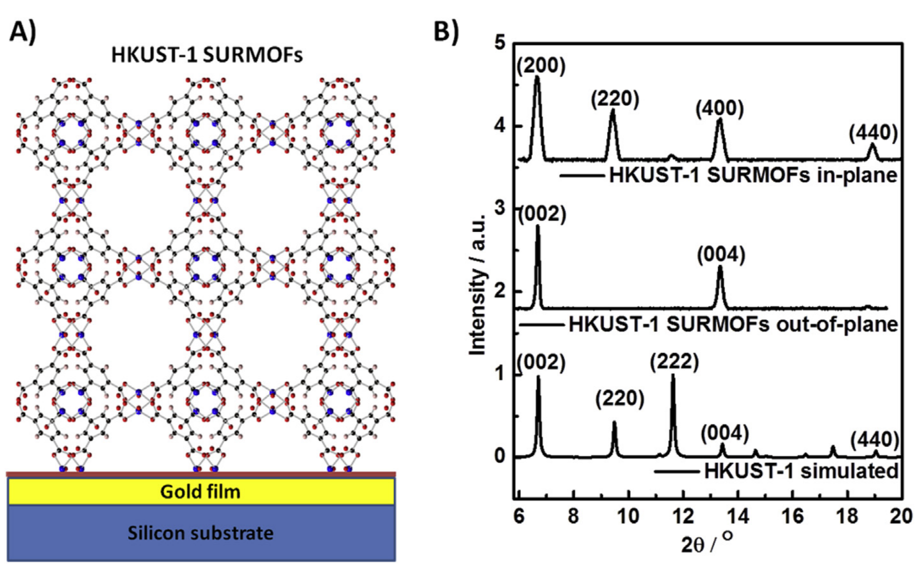

Fig. 1. A) Schematic structure of HKUST-1 SURMOFs grown on a MHDA-SAM-terminated (red line on the gold film) gold surfaces supported by silicon. B) In-plane and out-of-plane X-ray diffractograms recorded for HKUST-1 SURMOFs compared with the calculated diffractogram. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)