Surface-Anchored Metal-Organic Frameworks (SURMOFs)

SURMOFs represent a new class of highly porous and highly crystalline materials that may be used as host structures for molecules or nanoparticles with high application potential in gas storage systems, optical sensors, or catalytically active materials, to name a few examples. Metal-Organic Frameworks (MOFs) - in general - consist of two main components: metallic nodes and organic linker molecules. An automated layer-by-layer (LBL) deposition procedure [1] allows to deposit the metal compound and the linker molecules in an alternating fashion on chemically functionalized substrates (oxides, gold-coated substrates). The thickness of the layers is determined by the number of synthesis cycles while the size and chemical properties of the SURMOFs are defined by the used linker molecules. Different methods, e.g. spray or dip coating, are available for the SURMOF preparation. The application of additional treatments (e.g. ultrasonication), results in SURMOFs with high optical quality and high transparency. [2]

In contrast to MOF thin films prepared from powders deposited on substrates by painting or doctor-blade techniques, the SURMOFs are monolithic, highly oriented and exhibit a low density of defects. Due to these outstanding properties SURMOFs can be used not only as model system for studying crucial intrinsic properties of MOF materials, including diffusion of guest species and the formation of surface barriers (see [3] as a review) but also as model host substrates for nanoparticles [4] or molecules to investigate e.g. diffusion processes [5] or charge transport behavior [6]. After fabrication, SURMOFs are characterized by X-Ray diffraction (XRD, to verify crystallinity and growth orientation) and by IR reflection absorption spectroscopy (IRRAS, for chemical characterization)..

Contact

See KNMF website or contact the KNMF User Office.

Features

The following three different **SURMOF systems** are available:

- **HKUST-1**
  J. Am. Chem. Soc., 2007, 129 (49), pp 15118–15119
- **Cu(BDC)**
  Appl. Phys. Lett. 103, 091903 (2013)
  Scientific Reports 2, Article number: 921 (2012)
- **$Cu_2(BDC)_2$(dabco)**

The following types of **substrates** can be coated:

- SiO_2 wafers
- (Quartz) glass
- Porous oxides
- Au coated substrates (Si-wafer, glass, mica)

Limitations/constraints

- Substrate size should not exceed 20 mm x 20 mm
- Porous oxides substrates have to be delivered by the user

References

[1] O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer, C. Woll: Step-by-step route for the synthesis of metal-organic frameworks. *J. Am. Chem. Soc.* **129** (2007), 15118-15119.
[2] Z.-G. Gu, A. Pfriem, S. Hamsch, H. Breitwieser, J. Wohlgemuth, L. Heinke, H. Gliemann, C. Wöll: Transparent films of metal-organic frameworks for optical applications. *Microporous and Mesoporous Materials* **211** (2015), 82-87.
[3] J.L. Zhuang, A. Terfort, C. Wöll: Formation of oriented and patterned films of metal-organic frameworks by liquid phase epitaxy: A review. *Coordination Chemistry Reviews* **307**(2016), 391-424.
[4] W. Guo, Z. Chen, Ch. Yang, T. Neumann, Ch. Kübel, W. Wenzel, A. Welle, W. Pfleging, O. Shekhah, Ch. Wöll, E. Redel: Bi_2O_3 nanoparticles encapsulated in surface mounted metal–organic framework thin films. *Nanoscale* **8** (2016), 6468-6472.
[5] W. Zhou, C. Wöll, L. Heinke: Liquid- and gas-phase diffusion of ferrocene in thin films of metal-organic frameworks. *Materials* **8** (2015), 3767-3775.
[6] Liu, T. Wächter, A. Irmler, P.G. Weidler, H. Gliemann, F. Pauly, V. Mugnaini, M. Zharnikov, Ch. Wöll: Electric transport properties of surface-anchored metal-organic frameworks and the effect of ferrocene loading. *ACS Appl. Mater. Inter.*, **7** (2015), 9824-9830.

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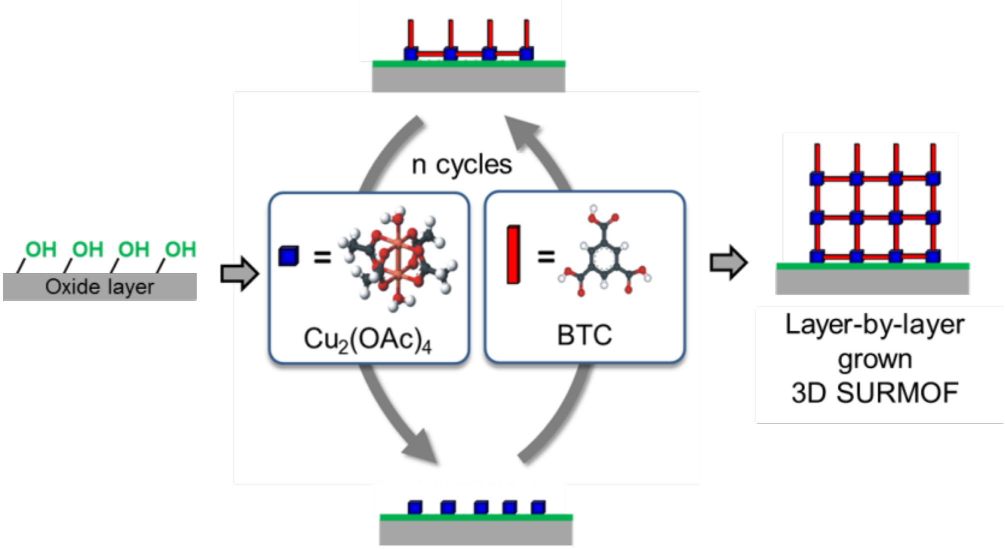
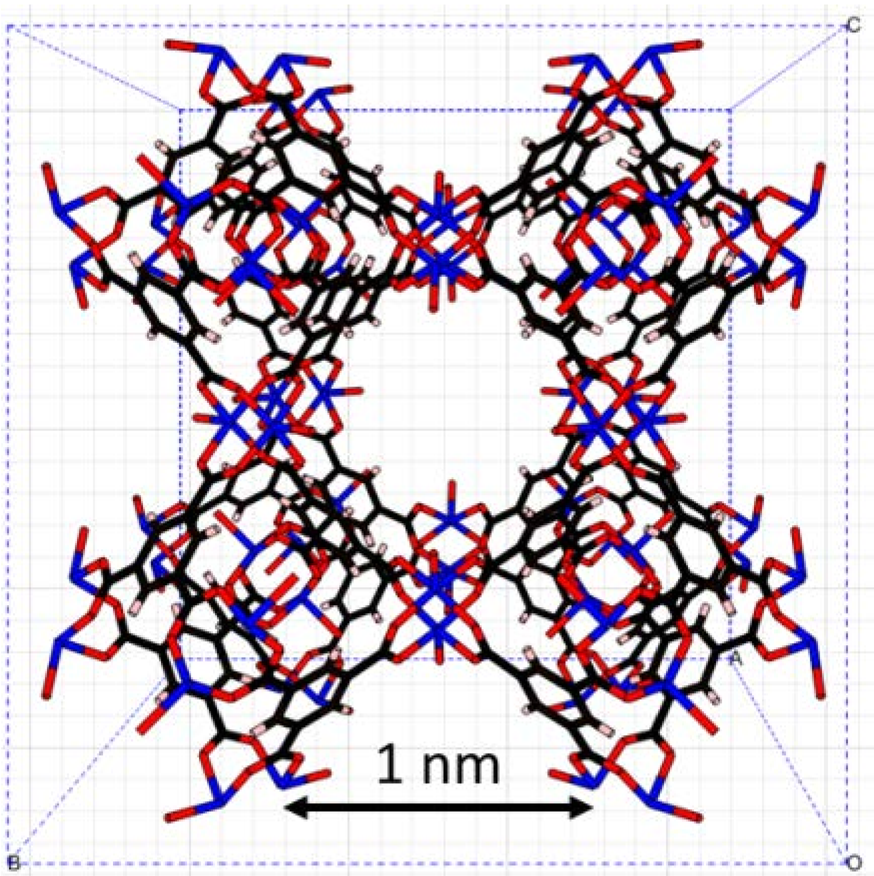
Layer-by-layer growth and typical properties of HKUST-1



Schematic layer-by-layer deposition process



Crystal structure for the example of HKUST-1 SURMOF

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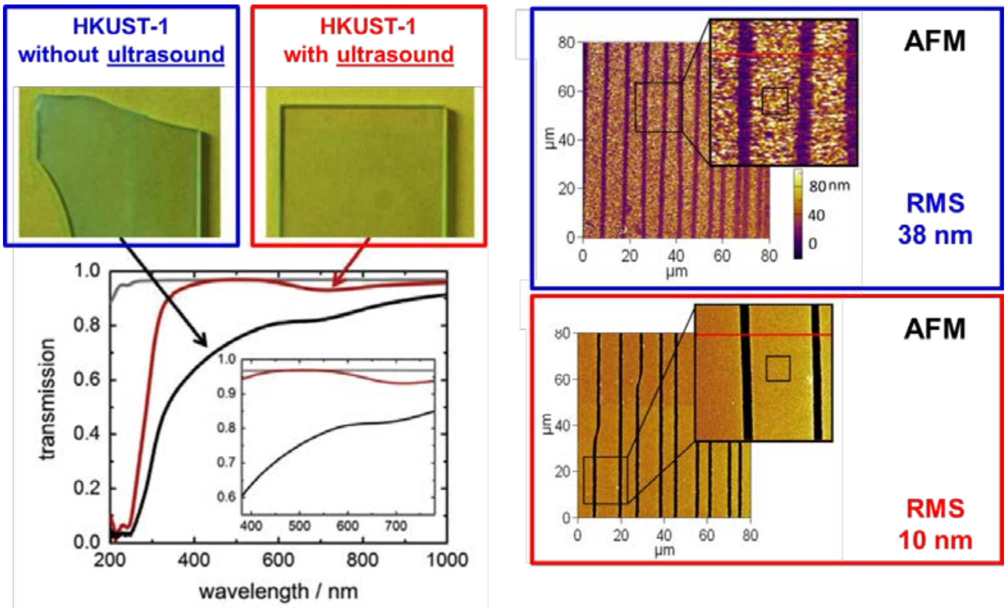
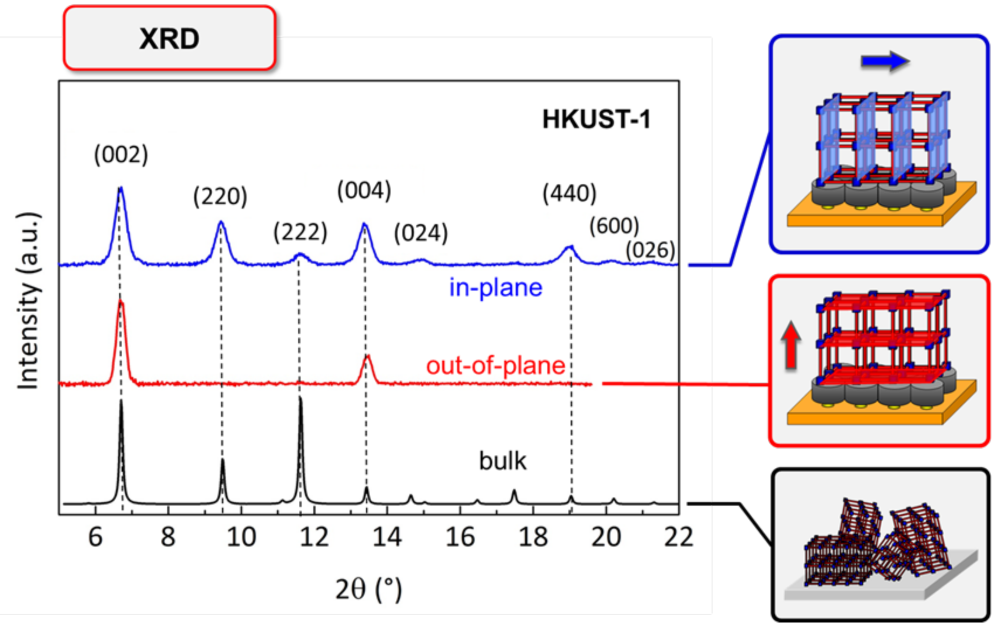


Typical optical and interfacial properties of an HKUST-1 SURMOF grown on a glass substrate w/o (blue) and with (red) ultrasound [2].



Typical XRD pattern of HKUST-1 SURMOF investigated in the in-plane and out-of-plane mode. The out-of-plane data proofs oriented growth of the SURMOF along the (100) direction.

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