



Surface-mounted metal-organic frameworks for applications in sensing and separation



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ABSTRACT

Thin films of metal-organic frameworks (MOFs) enable various applications ranging from membrane separations over sensor techniques to potential (micro-) electronic uses. Recent progresses of thin and homogenous surface-mounted MOF (SURMOF) films, which are prepared in a well-defined layer-by-layer fashion on a solid substrate surface, are highlighted in this review. Various substrate surfaces, ranging from plain metal, metal-oxide and polymer surfaces over metal-oxide membranes to magnetic nanoparticles, can be coated with SURMOFs. Multilayered SURMOF films with either identical or different MOF lattice constants or even different MOF structures were prepared, enabling the preparation of functional surface coatings. This allows, by incorporating photoswitchable azobenzene in the MOF structure, the preparation of multilayered, nanoporous films with remote-controllable properties. By means of crosslinking the SURMOF structure employing post-synthetic modifications, water stable thin films, SURGELS, can be prepared. Their thin and homogenous morphology also makes SURMOFs perfectly suited as coatings for electrochemical and electronic applications, where the small dielectric constant k as well as the option to tune the conductivity by loading the pores are very promising features of these porous solids. Furthermore, SURMOFs are very well suited for investigations of MOF-specific properties, since e.g. photoelectron spectroscopies can be applied to these thin films in a straightforward fashion. In additions, mass transfer and diffusion properties in MOFs can be studied for such thin films with high precision using a quartz-crystal microbalance (QCM).

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1. Introduction

Thin films of metal-organic frameworks (MOFs), a nanoporous, crystalline hybrid material composed of metal complexes and organic linker molecules [1], are a rapidly developing field with many potential applications [2]. These films can be prepared in many different ways. The preparation by spin-coating, dip-coating and hydro/solvothermal growth results in MOF layers composed of crystallites with a fairly large size distribution bound to the substrate surface [2–4]. These crystallites can also be overgrown to prepare pinhole-free films. A different approach is when the synthesis is directly on the surface, which is done by successively depositing the different components of this hybrid material. In this review article, we focus on thin, homogenous MOF films which are

prepared directly on the substrate surface in a layer-by-layer (LBL) fashion, employing liquid-phase epitaxy (LPE). These thin MOF films, called surface-mounted MOFs (SURMOFs), were introduced by Fischer and Wöll in 2007 [5,6]. Since the last reviews of SURMOFs in 2011 and 2012 [3,7,8], many new and interesting properties of the SURMOFs have been investigated. In the meantime, the LBL-MOF-synthesis (i.e. SURMOF) principle has also been successfully applied by many other research groups worldwide, e.g. by M. Allendorf et al. [9], J. Hupp et al. [10] and H. Kitagawa et al. [11], resulting in a number of very interesting new applications. Here, we concentrate on the SURMOF preparation on various substrate surfaces, ranging from plain metal, metal-oxide and polymer surfaces over metal-oxide membranes to magnetic nanoparticles, as well as on multilayered SURMOF films, which are composed of different SURMOF layers with either identical or different MOF lattice constants or even different MOF structures. By incorporating photoswitchable azobenzene in the MOF structure, functional, multilayered SURMOFs with remote-controllable properties can be prepared, allowing the remote-controlled release from a porous

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container. Crosslinking the SURMOF structure by employing post-synthetic modifications results in water-stable thin films, referred to as SURGELS. In addition to this, SURMOFs are a unique model system for MOFs, for instance enabling detailed investigations of the mass transfer in MOFs and unveiling the almost omnipresent phenomenon of surface barriers in MOFs. Chiral separation by using homochiral SURMOFs, i.e. SURMOFs with homochiral linkers, can also be studied. The option of tuning the electronic properties of MOFs in combination with the thin and homogenous morphology of SURMOFs also enables interesting electronic applications. A summary of all the SURMOF structures and substrates reviewed in this article is provided in Table 1.

First, we will briefly explain the synthesis of SURMOFs using the liquid-phase epitaxy method. For more detailed descriptions, we refer to previous review articles [7,8,12]. The modified substrate is

alternatively immersed in the solution of the metal ions and of the organic linker molecules, see Fig. 1. In between, the substrate surface is rinsed with pure solvent to remove any unreacted compounds from the surface. Surface modification can be carried out by using a number of different approaches. In the case of Au, the most appropriate method is to functionalize the Au surface with a self-assembled monolayer (SAM) made from organothiol monomers with a functional end group [13].

An example is the synthesis of HKUST-1 SURMOFs grown in [100] orientation on a 16-mercaptohexadecanoic acid (MHDA) SAM: The gold surface functionalized with the MHDA SAM, which has a functional –COOH head group, is immersed in the ethanolic copper(II) acetate (CuAc) solution, where the paddle-wheel-like CuAc compound chemically binds to the SAM. Subsequently, the sample surface is rinsed by ethanol and then the sample is

Table 1

Summary of SURMOF structures described in this review.

SURMOFs	Substrate	Investigations/Applications	Ref.
Cu ₃ (btc) ₂ or HKUST-1	–COOH and –OH terminated SAM on Au	Growth process and mechanism	[19]
	–COOH terminated SAM on Au	Defect density in SURMOF	[22]
	Rough surface of flexible synthetic polymers with –COOH and –NH ₂ terminated surface	Growth process	[30]
	–COOH terminated magnetic beads	MOF magnetic composites (magMOF)	[17]
	–COOH terminated SAM on Au	Mass transfer studies	[75]
	Modified Si substrate	Measuring dielectric constant	[86]
	–COOH terminated SAM on Au	Mechanical studies	[87]
SURMOF-2 Zn(bdc) (H ₂ O) and Cu(bdc) (H ₂ O)	–COOH terminated SAM on Au	Ferrocene-loaded SURMOF, conductivity investigation	[88]
	–COOH terminated SAM on Au	Europium-complex-loaded SURMOF as photonic antennas	[89]
	–COOH terminated SAM on Au	Structure different than structure obtained from solvothermal synthesis	[26]
Cu(bdc) Isorecticular SURMOF-2: Cu(bdc), Cu(bpdc), Cu(tpdc), Cu(qpdc), Cu(p(ep) ₂ dc), Cu(ppdc)	Modified Si substrate	Measuring dielectric constant	[86]
	–COOH terminated SAM on Au	Isorecticular SURMOF-2 series with structures different than structures obtained from solvothermal syntheses	[90]
Zn ₂ (bdc) ₂ (bipy)	–Pyridyl terminated SAM on Au	Suppression of framework interpenetration by LPE	[24]
Cu ₂ (ndc) ₂ (dabco)	–COOH, –pyridyl terminated SAM on Au	Crystal orientation control	[20]
	Macroporous alumina and titania membrane	Membrane-based separation	[33]
	–Pyridyl terminated SAM on Au	External surface modification by PSM	[40]
Cu ₂ (BME-bdc) ₂ (dabco)	–Pyridyl terminated SAM on Au	Diffusion coefficient and activation energy of ferrocene	[57]
	Macroporous alumina and titania membrane	Membrane-based separation	[33]
Cu ₂ (NH ₂ -bdc) ₂ (dabco) Zn ₂ (N ₃ -bdc) ₂ (dabco)	–OH terminated SAM on Au	Framework modification by PSM	[36]
	–OH terminated SAM on Au	Framework modification by click chemistry PSM	[39]
Zn ₂ (Dcam) ₂ (dabco) and Zn ₂ (Lcam) ₂ (dabco) Cu ₂ (Dcam) ₂ (dabco)	–Pyridyl terminated SAM on Au	Enantioselective adsorption	[79]
	–Pyridyl terminated SAM on Au	Enantiomer separation from a racemic mixture and circular dichroism	[80]
Cu(DA-SBDC)	–COOH terminated SAM on Au	Conversion of SURMOF to SURGEL	[41]
	–COOH terminated SAM on Au	SURGEL functionalization by thiol-yne click chemistry reaction	[42]
Zn ₄ O(dmcapz) ₃ , its derivatives and heterostructures Pillared-layer hetero-SURMOFs	–COOH terminated SAM on Au	Selective adsorption	[49,50]
	–Pyridyl terminated SAM on Au	Intermetallic heterostructures	[14]
	• Zn ₂ (ndc) ₂ (dabco) on Cu ₂ (ndc) ₂ (dabco)	Hetero-SURMOFs with layers of various dicarboxylate linkers	[20]
	• Cu ₂ (F ₄ bdc) ₂ (dabco) on Cu ₂ (ndc) ₂ (dabco)	Selective PSM in hetero-SURMOFs,	[51–53]
	• Zn ₂ (BME-bdc) ₂ (dabco) on Cu ₂ (ndc) ₂ (dabco)	Filter effects by spatial arrangement of SURMOF layers	
	• Cu ₂ (NH ₂ -bdc) ₂ (dabco) on Cu ₂ (bdc) ₂ (dabco); Cu ₂ (NH ₂ -bdc) ₂ (dabco) on Cu ₂ (ndc) ₂ (dabco); Cu ₂ (ndc) ₂ (dabco) on Cu ₂ (NH ₂ -bdc) ₂ (dabco) on Cu ₂ (bdc) ₂ (dabco)		
	Hetero-SURMOF: Cu ₂ (Azo-bpdc) ₂ (bipy) on Cu ₂ (bpdc) ₂ (bipy)	Photoswitchable azobenzene-containing SURMOF	[85]
	Hetero-SURMOF: Cu ₃ (btc) ₂ on Cu ₂ (ndc) ₂ (dabco)	Filter effects by spatial arrangement of SURMOF layers, different structures	[55]
	Isorecticular hetero-SURMOF-2	Hetero-SURMOF with large lattice mismatch	[56]

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