Creating Heterogeneous SURMOF Surfaces via Self-Assembly

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Catalysis is rapidly becoming a major application for metal-organic frameworks (MOFs).[1] As a result, MOF catalyst preparation is increasingly crucial to optimal catalyst design. An example of catalyst preparation is the anchoring of MOF on a (e.g. conductive) substrate, thereby creating a SURMOF. The anchoring can easily be performed using self-assembling monolayers (SAMs) of alkanethiols with headgroups functioning as nucleation points for MOF growth. SAMs have proven to yield excellent homogeneous SURMOFs,[2] yet homogeneous surfaces are typically not the most advantageous surfaces for catalysis. Catalytic reactions often thrive on materials with defect-rich surfaces possessing steps, kinks and edges. Therefore, in our research we manipulated the lateral stacking behavior of SAMs of alternate functionalities (promote/inhibit MOF/ZIF growth) to create thin-films of homogeneous MOF, MOF pillars and mixed MOF/ZIF surfaces (Fig. 1).

SAMs largely assemble due to Van der Waals forces between alkane chains.[3] We introduced alternate stacking forces through aromaticity and strongly interacting headgroups. By carefully mixing SAMs we could form chemically distinct domains. Domain-wise MOF growth resulting in nanopillars for photo-catalysis (Fig.1b,e) - photocatalytic lifetimes for novel MOF composites confirmed by transient absorption spectroscopy (TAS, Fig.1e inset) - and bi-functional surfaces (Fig. 1c,f) were thus synthesized. In order to chemically identify the separate domains, highly sensitive surface analysis techniques were required, such as Kelvin probe force microscopy (KPFM, Fig. 1e) or AFM-nano infrared spectroscopy (AFM-IR, Fig. 1f). In KPFM, the MOF islands showed a disparity in surface potential compared to the Au background, which can act as an internal standard to obtain accurate potentials for the different MOF/ZIF films in terms of metals and linkers, as well as orientation. AFM-IR gave detailed infrared information beyond the diffraction limit (<10 nm spatial resolution) allowing for nanoscale identification of MOF/ZIF species as well as defect sites. By combining these synthesis and characterization techniques, intricate (bifunctional) catalyst surfaces can be designed while circumventing the use of expensive “top-down” approaches.

Schematic visualizing a. homogeneous b. pillared and c. mixed SURMOF growth. d. AFM image of homogeneous SURMOF. Bulk IR in inset. e. High resolution KPFM of individual MOF islands. TAS in inset. f. AFM-IR map of mixed MOF-ZIF surface.


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