Gas adsorption studies using Surface-Anchored Metal-Organic Frameworks and Nanoplasmonic Sensing

Insplorion's nanoplasmonic sensing technique (NPS) exhibits an extremely high surface sensitivity for gas adsorption studies. In this application note it is shown how NPS can be used to monitor the gas adsorption to a Surface-Anchored Metal-Organic Framework (SURMOF).

Introduction

Metal-organic frameworks (MOFs) have in the recent years gained increasing attention due to their high porosity and gas selectivity. These characteristics make them interesting for several applications, including storage of gases like hydrogen and carbon dioxide, gas purification, gas separation, and in sensors. Insplorion's nanoplasmonic sensing technique (NPS), has previously been shown to display high sensitivity towards gas adsorption[1]. In this novel application, the surface sensitivity of NPS has been combined with the high surface area and selectivity of a MOF. Via a layer-by-layer (LbL) technique developed in the group of Prof. Wöll in 2007, an oriented surface anchored MOF can be grown on the surface of a flat substrate, creating a so called surface-anchored metal-organic framework (SURMOF). MOFs grown using LbL techniques have the advantage that they, unlike ordinary powder MOFs, do not have granular defects which, when present, inhibits homogenous adsorption throughout the material. As a proof of principle Insplorion's NPS sensors were coated with 5 layer and 15 layer HKUST-1[2] MOFs, respectively, and the adsorption of cyclohexane guest molecules was monitored.

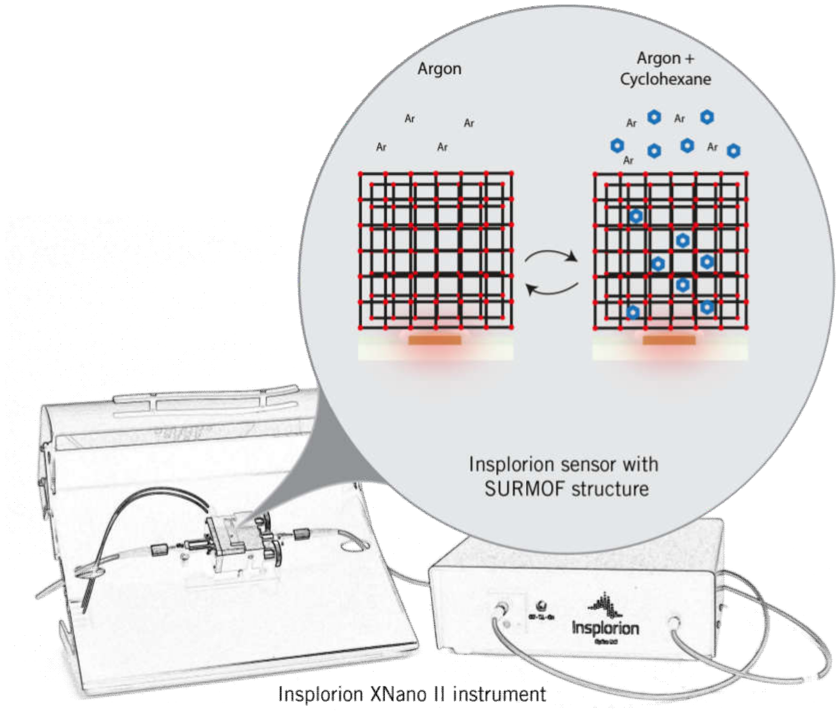

Figure 1. Insplorion sensors functionalized with a SURMOF. The metal-organic framework has the ability to host large amounts of guest molecules, in this case cyclohexane.

Method

Insplorion sensors, with a SiO_2 coating were used as substrates. First the sensor surface was treated in an oxygen plasma in order to functionalize the surface with -OH groups. After the functionalization step, the HKUST-1 was deposited on the surface via an LbL spray technique. The desired thickness was reached through repetition of the LbL procedure. Thicknesses of approximately 40 (5 layer) and 120 (15 layer) nm were

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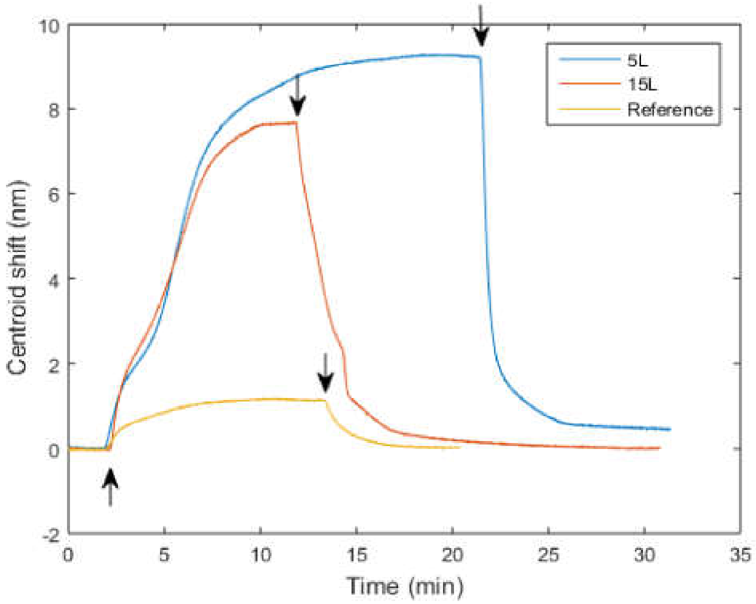

Figur 2. Centroid shift as a function of time and HKUST-1 layer thickness. The first arrow marks the introduction of cyclohexan into the system. The following arrows marks the switch to pure argon.

used. The measurement was made in the Insplorion Xnano instrument seen in Figure 1. The guest molecules (cyclohexan) were introduced to the framework using argon as a carrier gas. The carrier gas was bubbled through a washing bottle filled with cyclohexane and afterwards guided into the measurement chamber. During each measurement, the centroid position of the Au NPs on the sensor surface was monitored in real-time. As the SURMOF was loaded with molecules, the centroid position shifted to a longer wavelength (redshift). After loading the MOF with cyclohexane, the measurement cell was flushed with pure argon to unload the molecules from the MOF.

Results

The main results are shown in Figure 2. The graph shows the spectral shift of the centroid position upon loading and unloading of the SURMOF. Loading caused a redshift of the centroid position due to the increased refractive index in the proximity of the NPS sensors. A bare, uncoated sensor was used as a reference. On the reference sensor, only a thin layer of the guest molecules adsorbed to the surface, causing a slight redshift. On the contrary, performing the same measurement on sensors coated with HKUST-1 yields much larger responses since the SURMOF can store large amounts of molecules. The difference between the recorded signals from the five-layer structure and the fifteen-layer structure is very small since the probe depth of NPS is on the order of a few tens of nanometers and thus does not extend much beyond the thickness of the five-layer SURMOF. An increase of the SURMOF thickness to fifteen layers therefore has little effect on the NPS signal. After cyclohexane adsorption, the cell was flushed with argon resulting in a shift of the centroid position back to its original position, indicating that all of the guest molecules leave the MOF.

Conclusion

Insplorion's NPS technology is a promising tool to study gas adsorption to MOFs. The high surface sensitivity makes it possible to selectively monitor the gas adsorption to the inner layers of SURMOFs.

This application note is a short summary of a study performed by researchers at the Institute of Functional Interfaces, Karlsruhe Institute of Technology, Germany. A more detailed description of the experiment, theory and results can be found in [3].

References

[1] *UV-Visible and Plasmonic Nanospectroscopy of the CO_2 Adsorption Energetics in A Microporous Polymer, Ferry A.A. Nugroho, Chao Xu, Niklas Hedin, and Christoph Langhammer, Analytical Chemistry. 2015, DOI:10.1021/acs.analchem.5b03108*

[2] *A chemically functionalizable nanoporous material, Chui SS, Lo SM, Charmant JP, Orpen AG, Williams ID, Science (1999) 283, 1148-1150*

[3] *Surface-Anchored Metal-Organic Frameworks – SURMOFs: A New Material Platform for Sensors, Himanshu Gulatio, Peter Lindeman, Lars Heinke, Jianxi Liu, Manuel Tsotsalas, Christof Wöll, Hartmut Gliemann, 2015, DOI 10.5162/12dss2015/P7.6.*