Application Note # 112

In Situ Monitoring of Metal-Organic Framework Assembly with MP-SPR

Multi-Parametric Surface Plasmon Resonance (MP-SPR) instrument was used for precise in situ monitoring of the Metal Organic Framework (MOF) assembly of [$Cu_3BTC_2(H_2O)n$]. MOF layer complex refractive index (RI) was calculated in two different media, in air and in ethanol. Based on known layer thickness (1.3nm/bilayer) complex RI was determined to be in ethanol ñ = 1.5085 + i 0.0065 and in air ñ = 3.784 + i 0.0123.

Introduction

Metal-organic frameworks (MOFs) are crystalline supramolecular assemblies that are built up from precisely defined subunits by coordination or covalent interactions [1]. MOFs are usually highly porous, and they offer a wide range of applications where incorporation of guest molecules are needed. Applications include fuel storage, catalysis, drug delivery and gas sensing. A layer-by-layer (LbL) method for building MOF structures has been introduced, and it offers more control on the structure. [1,2]

SPR phenomenon is based on free electrons resonating at a metal surface, which are excited with light. There is an absorption maximum (called as peak minimum) as a function of the angle of the incident light, and the SPR phenomenon is highly dependent on the dielectric constant near the metal surface. Any changes near the surface, such as deposition of new layer, change the peak minimum angle. Due to the MP-SPR unique optical setup instrument can be utilized for determining not only affinity and kinetic of the interaction but also layer properties like thickness and refractive index with high precision.

MP-SRP instrument allows measurements in Fixed angle mode where intensity changes in specific angle of the incident light is monitored as well as measurements in Angular scan mode where whole SPR curve can be monitored during measurement.

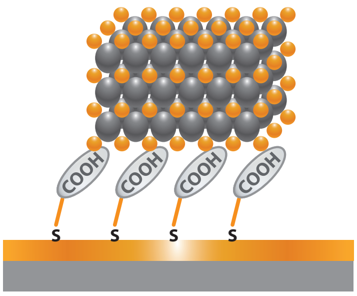

Figure 1. Metal Organic Framework (MOF) deposited on a gold sensor slide with self-assembled monolayer (SAM).

Materials and Methods

A self-assembled monolayer (SAM) of 11-mercaptoundecanoic acid (5mM in ethanol, 20 h in room temperature) was prepared on a gold sensor slide for the MP-SPR measurement. The running solvent during the experiment was ethanol. The first injection was 1 mM copper(II) acetate ($CuAC_2$) in ethanol followed by injection of 0.05 mM of benzene-1,3,5 -tricarboxylic acid (BTC) (Fig. 1). The LbL assembly was continued by sequential injections of 0.2 mM $CuAC_2$ and 0.05 mM BTC until 8 bilayers had been created on the sensor surface. The assembly process was monitored both in fixed angle and angular scan measurement mode with SPR Navi™ 200 (Figure 2).

Results and Discussion

The sensogram from Fixed Angle measurement and the sensogram of SPR peak minimum from Angular Scan measurement (Fig.2) were in good agreement with previous studies [3]. Since the MP-SPR instruments allows collection of the complete SPR curve it is possible to determine the optical complex refractive index (ñ = n + ik) of the formed MOF assembly. The whole SPR curve for the final and initial states of the MOF assembly in both ethanol and air are shown in Figure 3. Measurements in air and in liquid can be easily done without any change in the SPR Navi™ instrument setup. MOF is a light absorbing layer and this causes the peak minimum intensity to go upwards after MOF deposition.

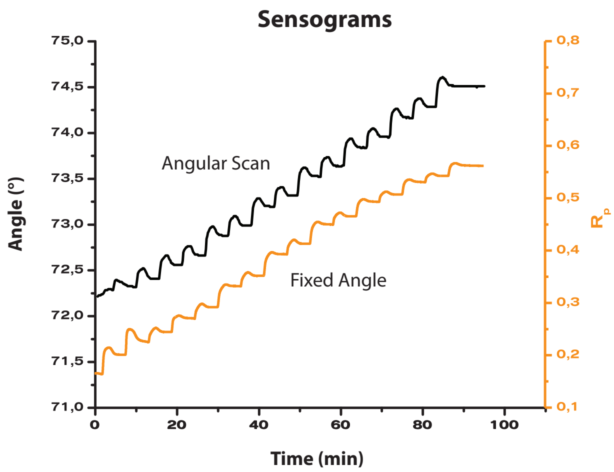

Figure 2. SPR sensogram from both Fixed Angle experiment (orange curve and right hand y-axis), and Angular Scan experiment (black curve and left hand y-axis)

Excellence in Surface Plasmon Resonance
BioNavis

Oy BioNavis Ltd.
Elopellontie 3 C
33470 Ylöjärvi
Finland

Tel : +358 10 271 5030
e-mail : info@bionavis.com
www.bionavis.com

The thickness of a [Cu3BTC2(H2O)n] MOF has previously been determined by atomic force microscopy to be 1.3 nm per bilayer [4]. By using this thickness, we obtained a complex refractive index of ñ = 1.5085 +i 0.0065 for the 8 bilayer of MOF in ethanol. The other bilayers were modelled for n assuming a constant k and layer thickness increment. As a result from this analysis the optical thickness (nd = n*d) vs. layer number (Figure 4A) and the optical thickness increment (ndn-ndn-1) (Figure 4B) were plotted. Figure 4A shows a very good linearity of the optical thickness vs. layer number. However, there is a slight difference in the layer growth increment in the beginning of the experiment (Figure 4B). The thickness increment for the first layer is 1.71, but starts approaching a constant value already from the third bilayer. The first few layers do not grow perfectly because of the surface roughness and imperfect complex formation on the first layer. This could indicate that the MOF grows as islands on the surface in the beginning. The optical constants for the dried 8 bilayer MOF assembly were also modelled in air in order to compare structural differences for a wet and dry MOF assembly. Assuming the same layer thickness as for the MOF in ethanol (i.e. 10.4 nm) the complex refractive index of the MOF in air was modelled to be ñ = 3.784 + i 0.0123. The differences in ñ between air and ethanol mediums are probably due to differences in the lattice structure.

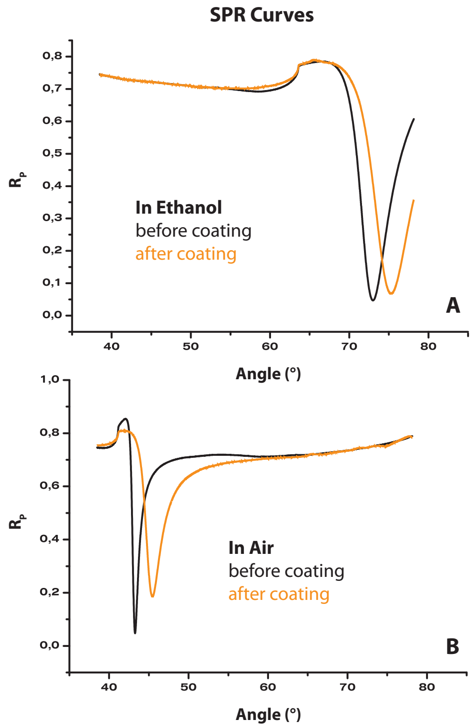

Figure 3. The SPR spectra of the gold slide sensor before (black curve) and after (orange curve) MOF assembly in ethanol (3a) and in air (3b).

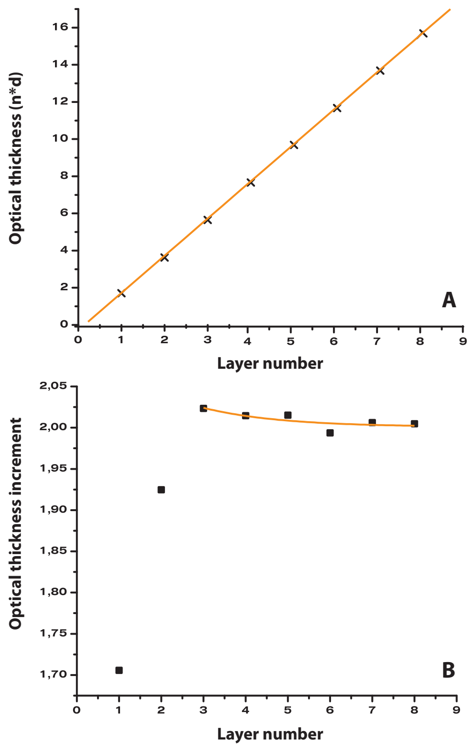

Figure 4. A) Optical thickness versus layer number. B) Optical thickness increment versus layer number

Conclusions

MP-SPR is a powerful instrument for monitoring in situ build-up of metal organic framework assemblies. The unique MP-SPR setup enables monitoring of light absorption on the surface and therefore it can be utilized to characterize light absorptive samples and layers. The instrument enables optical characterization, i.e. complex refractive index determination, of the same MOF assembly both in air and in organic liquid without any change in the instrument setup. MP-SPR instrument and MOF characterization can be utilized in various research areas such as drug delivery and sensor development as well as gas sensing and storage.

With MP-SPR instrument it is also possible to determine both unique refractive index (RI) and thickness of deposited layers without prior knowledge of the RI or the thickness of the layer. For this, see BioNavis Application Note 128.

References:

(1) Shekhah, O. et al. Nature Materials 2009, 8, 481

(2) Shekhah, O. et al. J. Am. Chem. Soc. 2007, 129, 15118

(3) Schasfoort, R. B. M., Tudos, A. J., Handbook of Surface Plasmon Resonance, RSC 2008

(4) Munuera, C. et al. Phys. Chem. Chem. Phys. 2008, 10, 7257

Recommended instrumentation for reference assay experiments
SPR Navi™ 200, 210A or 220A
Sensor surfaces: Au or other metal
Software: SPR Navi™ Control, SPR Navi™ DataViewer, SPR Navi™ LayerSolver

Oy BioNavis Ltd.
Elopellontie 3 C
33470 Ylöjärvi
Finland

Tel : +358 10 271 5030
e-mail : info@bionavis.com
www.bionavis.com