Metal-organic framework (MOF) characterization using MP-SPR

Metal-polyphenol complex (MPC) film deposition was monitored in situ using Multi-Parametric Surface Plasmon Resonance (MP-SPR). The sequential deposition of Tannic Acid (TA) and Fe(III) ions was performed up till 8 cycles. Depositions were measured at two wavelengths (670 nm and 785 nm), and thickness and refractive index were determined using LayerSolver™ software. The first three layers were initial layers, forming only about 2 nm MOF layer on the surface. Thickness of all the 8 MOF layers was 21.0 nm and the refractive index was 1.435 (at 670 nm). Fe(III) and TA formed an amorphous MOF layer.

Figure 1. Metal-organic framework (MOF) layer-by-layer deposition on a polyethylenimine (PEI) coated gold sensor slide. Eight tannic acid and Fe (III) layers were deposited *in situ*.

Introduction

Metal organic frameworks (MOF) are usually highly porous structures being utilized in a wide range of applications, including fuel storage, catalysis, drug delivery and gas sensing. Tannic acid (TA) is a highmolecular- weight polyphenolic substance that has a central glucose core and five digalloyl ester groups covalently attached to the core. This type of structure enables interactions with a variety of materials via multiple reaction pathways. TA can form a highly stable complex with iron(III) ions, the complex formation being highly pH-dependent (Ejima *et al*. 2013, Hajim *et al*, 2014).

The MP-SPR instruments can perform measurements in a wide angular range (40-78 degrees) and can record SPR curves at more than one wavelength, thus making the instrument an excellent tool for MOF layer characterization. MP-SPR additionally measures molecular adsorption in real-time. The same measurement also allows layer thickness and refractive indexes to be calculated. Additionally, MP-SPR allows measurements in air and in liquid without any changes in the instrument setup, and the system is also compatible with a variety of organic liquids/solvents.

Materials and methods

Gold sensor slides were cleaned with $NH_3/H_2O_2/H_2O$ (1:1:5 v/v) solution, rinsed with water, and pre-coated with polyethylenimine (PEI) *ex situ* using 0.2 mg/mL PEI solution containing 0.3M NaCl.

Measurements were performed using MP-SPR Navi™ 220A NAALI instrument equipped with two wavelengths (L-option). Altering layers of tannic acid 0.2 mg/mL, pH= 7-8 and $FeCl_3$ 0.05 mg/mL, pH=3.2 were deposited *in situ*. Multilayers were formed in two flow channels (FC1 and FC2) using serial injections. Solutions changed slowly color over time indicating chemical reaction, however, data presented here were obtained using freshly prepared solutions.
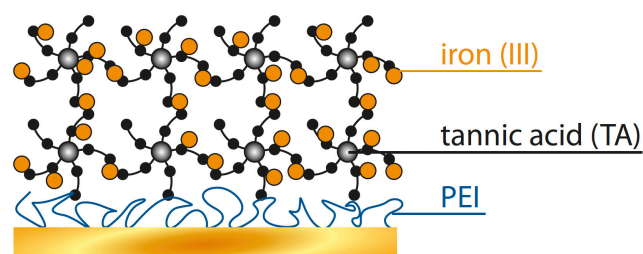
Results and discussion

Metal-organic framework assembly was monitored in real-time using an MP-SPR instrument (Figure 2). It was noticed that during the first three Fe(III) + TA layers the calculated layer refractive index increased indicating that film was mainly packing. Initially only thin MOF layers were formed on top of PEI layer, and the first three deposition cycles gave total thickness of 1.9 and 2.1 nm respectively for FC1 and FC2. The sensogram of the deposition also showed that Fe(III) starts to clearly bind more strongly after the three first injections (Figure 2, time point 127 min).
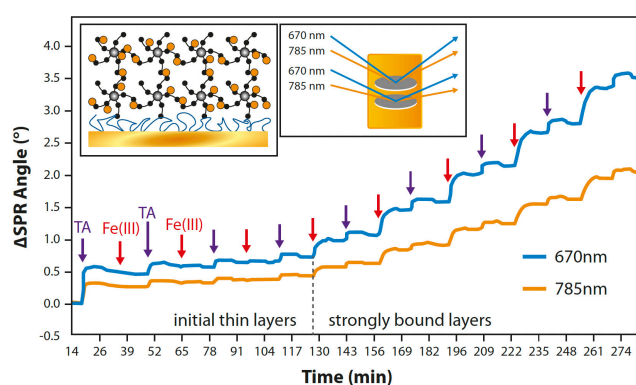

Figure 2. Real-time monitoring of metal-organic framework assembly. Altering layers of tannic acid (TA) and Iron (III) were deposited. Deposition was measured simultaneously using two different wavelengths (670 nm and 785 nm). As expected, using 670 nm wavelength results in larger shift in SPR curve compared to 785nm wavelength. Stronger binding of Iron (III) can be detected after the third Fe(III) injection (at time point 127 min).

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Besides an increase in minimum angle (shift to the right), also the minimum intensity decreased during the first three layers (Figure 3) as can be seen from the full SPR curve. This indicates increase in smoothness of the surface during the initial layer formation. Same trend was detected in both of the measurement channels.

After the three initial layers MOF starts to grow rapidly (Figure 2). Thicknesses of the 8 TA + Fe(III) layers were 31.6 nm (FC1) and 21.0 nm (FC2) and the refractive indexes were 1.487 and 1.435 respectively (at 670nm wavelength) (Figure 4). Refractive index of the 8 bilayer MOF is rather low for phenolic compounds, however this indicates highly porous structure of the MOF with low mass density. Despite the presence of the Fe (III) component in the layer, the extinction coefficient (k) was characterized to be zero, which may be due to the amorphous nature of layer and the low absorption coefficient of Fe (III) at the used wavelengths.

Difference in the layer formation between the two channels was observed. The same sample flowed through both of the two fluidic channels but a noticeably lower thickness of the layer was characterized for the second channel. As some of the sample has bound in the first channel, the remaining lower concentration of the samples might influence deposition of the layers in the second channel. However, average bilayer thicknesses were only slightly higher than reported in the literature: 2.2 nm in water (Rahim *et al.* (2014) QCM), and 2.6 nm/layer (Ejima *et al.* (2013) AFM).

Additionally, it was noticed that TA + Fe(III) layers could not be removed from the sensor surface with typical cleaning agents such as Hellmanex III or acetic acid. However, EDTA and NaOH with NaCl were suitable reagents to destroy the MOF and regenerate the sensor surface.

Conclusions

It was demonstrated that Multi-Parametric Surface Plasmon Resonance (MP-SPR) can follow metal-organic framework (MOF) assembly in real-time, and that the thickness and refractive index of the formed layers can be calculated using two wavelength data and LayerSolver™ software. Without any change in the instrument setup, MP-SPR can also be used for measurements in organic liquids such as ethanol, acetonitrile, and 2-propanol. Additionally to measurements in liquid, MP-SPR allows measurements in air or in other gaseous environments.

MP-SPR can measure also layer properties of crystalline MOF structures. See how MP-SPR was utilized to measure Cu3BTC2(H2O)n MOF in air and in ethanol (Application Note #112).

Furthermore see how simultaneous electrochemical (EC) and MP-SPR measurements are performed (Application Note #142).

References:

Ejima *et al*., Science, 2013
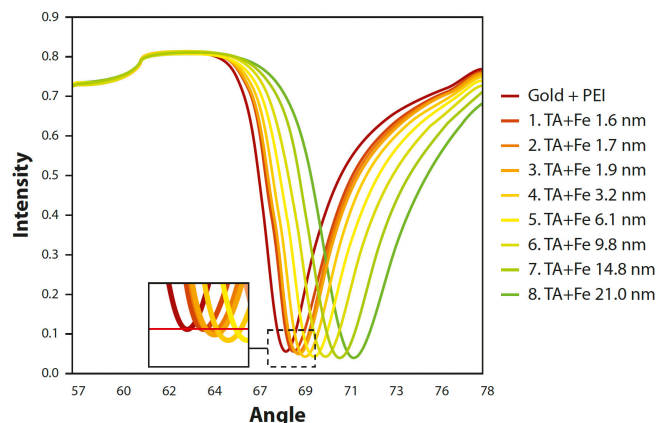Rahim *et al*., Chemistry of Materials, 2014

Figure 3. Full SPR curve measured using 670nm wavelength, before MOF deposition and after each bilayer up to eight layers. SPR curve is shifting to the right as layers are being formed. Interestingly, during first three layers peak minimum intensity is slightly declining (see inset) due to decreased roughness of the surface. The same phenomenon is detected in both independent channels.
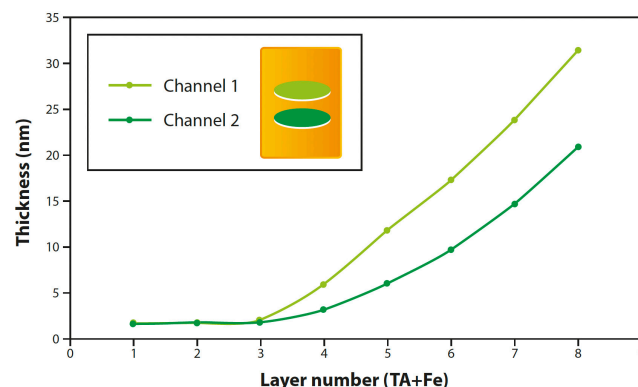

Figure 4. Metal organic framework (MOF) layers thicknesses after each bilayer up to eight layers. Lower thickness of the layer was characterized for the second channel after the initial layers.

Recommended instrumentation for reference assay experiments

MP-SPR Navi™ 200 OTSO, 210A VASA or 220A NAALI with additional wavelength -L

Sensor surface: Au, other metal or inorganic coating

Software: MP-SPR Navi™ Controller, DataViewer and LayerSolver™ for MP-SPR Navi™

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