Synthesis of Metal Organic Frameworks thin films for electrochemical applications using molecular layer deposition

Atomic layer deposition is a unique technique for deposition of conformal and homogeneous thin films. Its simplicity, reproducibility and the high conformality of the as-deposited films make it a promising deposition process[1]. Briefly, it is based on a reaction between precursor materials, which are separated into successive surface reactions. In this manner, the reactants are kept separated and react with surface species in a self-limiting process, i.e. without the presence of a gas phase reaction, differentiating it from the chemical vapor deposition technique. Each surface reaction is followed by a purge step to remove the unreacted precursor and the by-product. The succession of self-limited reaction and purge constitute a cycle (Figure 1). The growth per cycle is defined as the thickness of the film deposited in one full cycle. Due to the self-limited reactions, the thickness of the as-deposited film is simply controlled by the number of cycles, up to the atomic scale level.

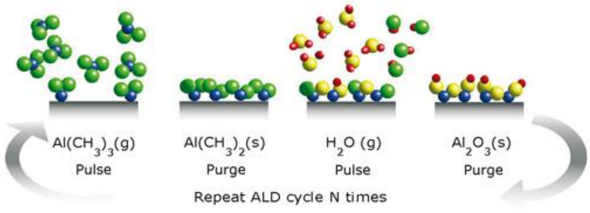

Figure 1. Schematic of an ALD cycle: example of Al_2O_3 deposition from $Al(CH_3)_3$ and H_2O. *Step 1:* pulse of the reactant 1, $Al(CH_3)_3$, leading to its absorption on the surface. *Step 2:* purge of the unreacted precursor and of the by-products. *Step 2:* pulse of the reactant 2, H_2O, which reacts with the surface species created by precursor 1. *Step 4:* purge of the unreacted precursor 2 and of the by-products. Reproduced from "J. Pimenoff, *Vak. Forsch. Prax.*, **2012**, 24 (6), 10-13".

ALD has already proved to be suitable for elaboration of functional structured material, applied for instance in energy and environment domains. Indeed, ALD processes exist for a large variety of material classes, such as metals, oxides, nitrides, sulfides and phosphates. It has lately been adapted to deposit organic polymer and hybrid thin films. This approach is called Molecular Layer Deposition (MLD). Recently, thin films of Metal Organic Frameworks (MOFs) have been also reported using ALD/MLD technique [2-4] but this process is still complex and the structural control and growth parameters are not clearly understood.

In our group we are developing MOFs based on redox active ligands [5,6] and we study their activity in energy related applications such as electrocatalysis of oxygen reduction reaction used in polymer electrolyte membrane fuel cells. However, usually these materials are obtained as bulk powders or single crystals. Therefore, true implementation of MOFs in energy-related technologies offers a tremendous potential but requires an extra-effort in the development of fabrication methods that are compatible with industrial processes. A gap has to be filled to move from individual crystals or powders toward continuous high-quality films. For this purpose, a solvent-free molecular layer deposition (MLD) approach is proposed to develop building films with molecular scale precision. This process is strongly innovative in the field of coordination polymer assembling

In the course of the research project, we are first aiming to synthesize and to explore the very fine structuration of MOFs using MLD. Attention will be given to the substrate influence on the crystallinity and epitaxial growth of the as-grown MOFs. An important step will be the study of the lattice influence for a MOF phase grown on a carefully chosen crystalline substrate orientation. Then MLD of redox active MOFs will be aimed. First tests will be performed with known sublimable porphyrinic ligands, and then other systems will be considered such as phthalocyanines and dithiolenes. MLD structuration brings the greatest opportunity to foresee molecular solids based on several redox active linkers combined inside one crystallite in a totally controllable way. This technique allows for a great advantage to avoid the equilibrated reactions in solution and opens completely new opportunities for MOFs structural controlling. This structuration control level is for now unexplored therefore this ambitious project opens the path to pioneering structures. In case where redox-active thin films are obtained, they will be tested for the electrocatalytic activity and the influence of the film structuration on the performance and electrochemical stability will be outlined.

This research is related to the JCJC ANR-STREAM project; therefore funds for lab supplies, characterization techniques and results dissimilation (conference participations) will be available. It will also benefit from a recent collaboration with LEPMI laboratory in Grenoble (Dr. Fréderic Maillard), expert in electrocatalytic materials studies.

Techniques:

Synthesis techniques: atomic layer deposition, inert atmosphere lab work, organic synthesis, coordination chemistry, solvothermal synthesis.

Characterizations: X-ray diffraction (powder and single crystal), ellipsometry, XRR, spectroscopies (NMR, IR, UV-vis), microscopies (AFM, SEM), sorption isotherms measurements, electrochemistry (solution and solid state).

Skills:

Highly motivated candidates careful with research work and having excellent communication and organizational skills are encouraged to apply. Knowledge in coordination chemistry and general scientific interest is highly appreciated.

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