Emerging Materials
Room Van Eyck - Session EM3-WeA
Hybrid Coatings

Moderators: Christophe Detavernier, Ghent University, Belgium, Mark Losego, Georgia Institute of Technology

4:00pm **EM3-WeA-11 Photoactive Hybrid Materials by MLD***, **Ola Nilsen**, P. Hansen,* University of Oslo, Norway **INVITED**

The sequential methodology of ALD/MLD allows for combinations of a remarkable wide range materials. This can be exploited in construction of photoactive materials, particularly for those based on multi-step processes like down and upconversion. Such materials relies on efficient processes for both absorbers, emitters and transfer of excited states while limiting non-radiative decay. It is clear that optimizing all properties simultaneously is not possible within a single material class.

With the ALD/MLD approach, we can combine highly absorbing organic molecules with fluorides and oxides and many more. By such manner, we have achieved complete energy transfer from the organic molecule terephthalic acid to Sm3+ without quenching. We also show drastic suppression of concentration quenching of multilayered structures of lanthanides as compared to solid solutions by confining energy migration in 2D planes. The flexibility of the MLD approach allows for exploration combinations of absorbers and emitters with a large variation in chemistry. Although one may be limited in the size of accessible molecules via the gas phase, the range may be quite large. This way of design allows combinations of otherwise incompatible species, both with respect to normally incompatible synthesis requirements and in controlling energy transfer and quenching routes.

4:30pm **EM3-WeA-13 Cerium (III) based Hybrid Inorganic-Organic Thin Films by ALD/MLD***, **Parmish Kaur**,* Ruhr University Bochum, Germany*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; J. Wree,* Ruhr University Bochum, Germany*; R. Ghiyasi, M. Safdar,* Aalto University, Finland*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; M. Karppinen,* Aalto University, Finland*; A. Devi,* Ruhr University Bochum, Germany

Ce-based hybrid materials are projected to be promising for applications such as catalysis, sensors, information storage, luminescent materials to name a few. However, they have been mainly developed by classical routes such as solvothermal and hydrothermal synthesis and thus suffer a major disadvantage of unwanted solvent molecules being trapped in the hybrid materials. Atomic/molecular layer deposition (ALD/MLD) is a solvent-free, gas-phase deposition technique for the deposition of hybrid organic-inorganic thin films which gives precise control over thickness, composition, and uniformity over large area substrates. Although one of the key factors of a well-functioning ALD/MLD process is the compatibility of the employed organic and inorganic precursors in terms of volatility, thermal stability, and reactivity and this aspect hasn't been thoroughly investigated.

We have performed a systematic study to find compatible Ce and organic precursors for the growth of Ce-based hybrid thin films. This was realized by in-depth characterization of precursors, processes and supporting the findings by theoretical investigations using density functional theory (DFT). Thermal analysis studies showed that the precursors [Ce(dpdmg)$_3$], terephthalic acid (TPA), and hydroquinone (HQ) are sufficiently volatile and thermally stable to be deposited at 200 °C. Additionally, the reactivity of the precursors was modelled by DFT, which revealed the favourable reaction between inorganic and organic precursors. Thus, the combination of the chosen precursors was found to be compatible in terms of their matching physicochemical properties. The Ce-based hybrid thin films were deposited using [Ce(dpdmg)$_3$] as a source for Ce, while two different organic precursors, namely TPA and HQ, were tested as organic precursors yielding Ce-TPA and Ce-HQ hybrid thin films. The growth rate for Ce-TPA hybrid films was 5.4 Å cycle^{-1} and for Ce-HQ hybrid films it was 4.8 Å cycle^{-1} on Si(100) at a deposition temperature of 200 °C. FTIR studies confirmed the successful deprotonation of the organic precursors, the presence of metal-oxygen bonding, and the benzene ring vibrations in the hybrid films. Additionally, the Bader charge calculations predicted the oxidation state of the cerium in the films to be +3 which was further confirmed experimentally by XPS studies. Furthermore, XPS analysis confirmed the successful formation of Ce-O bonds. UV-Vis spectroscopy showed the π-π* transitions and LMCT transition present in the films, while the films are also UV absorbing. Hence, Ce-based hybrid thin films can be promising as redox-active or UV-absorbing materials.

4:45pm **EM3-WeA-14 Modifying the Physico-Chemical Properties of Polymer Nanofiltration Membranes with Metal Oxide ALD***, **Kirti Sankhala**, T. Segal-Peretz ,* Technion, Israel

Atomic layer deposition (ALD) is an emerging technology to tune the surface chemistry of membranes by providing conformal, smooth, and ultrathin coatings of various materials, such as metal oxides.[1,2,3] The addition of an ultra-thin layer of metal oxides on a negatively charged polymer membrane surface offers enhanced surface energy and hydrophilicity with a possibility to fine-tune the pore size and reduce surface roughness.[4]

In this work, we enhance the chemical and physical properties of commercially available NF270 nanofiltration membranesby tin dioxide (SnO_2) coating via ALD. SnO_2 ALD was selected due to the high hydrophilicity and positive surface charge of SnO_2 among various metal oxides.[5] In nanofiltration, the separations at the atomic or molecular scale are strongly influenced by electrostatic interactions and play a critical role in membrane performance. As ALD provides a conformal and nonporous coating layer, applying a large number of ALD cycles inevitably leads to pore blocking. However, a small number of ALD cycles (< 20) enables tuning of both the pore size and the pore chemistry.[6]Several cycles of SnO_2 ALD, providing ca. 1-3 nm thick coating,increases the membrane's hydrophilicity, decreases its roughness, and reduces negative surface charges. This coating leads to higher salt rejection and salt selectivity with a slight decrease in membrane permeability. The morphological details of the hybrid inorganic-organic membranes obtained using scanning and transmission electron microscopies shed light on the conformal growth of SnO_2 ALD on the nanofiltration membranes.

References

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5:00pm **EM3-WeA-15 Modelling of the Growth of Al_2O_3-Based Hybrid Films: Role of Terminal Groups in Aromatic Molecules***, **Arbresha Muriqi**,* Tyndall National Institute, University College Cork, Ireland*; M. Karppinen,* Aalto University, Finland*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland

Hybrid organic-inorganic materials fabricated using Molecular Layer Deposition (MLD) display unique properties and hold great promise for many technological applications. Much has been done in developing different MLD processes but much less is known about the growth mechanism in MLD films.

In this study we use first principles density functional theory (DFT) to investigate in detail the growth mechanism of hybrid films of aluminium oxide and aromatic molecules with different terminal groups deposited by MLD. We explore the reactions between the post-$Al(CH_3)_3$ (TMA) pulse methyl-terminated Al_2O_3 surface and homo- or hetero-bifunctional aromatic molecules with hydroxy (OH) and/or amino (NH_2) terminal groups: hydroquinone (HQ), p-phenylenediamine (PD) and 4-aminophenol (AP). DFT calculations show that the aromatic molecules bind favorably to TMA fragments via formation of Al-O, Al-N bonds and loss of CH_4. Importantly it is most favorable for the aromatic molecules to orient in an upright configuration, by avoiding the unwanted double reactions found for aliphaic diols, which will lead to thicker and more flexible hybrid films. We calculated a higher reactivity of the OH group with TMA compared to NH_2, However, aromatic molecules terminated with NH_2 groups are still an option to promote the film growth. We also explore the MLD chemistry with functionalised aromatic molecules to examine the influence of phenyl functionalization on the MLD chemistry. We found that we can modify the core of the aromatic molecules to target particular properties using specific chemical groups which promote the deposition of thicker and more stable hybrid films. Finally, we examine the reactions between the methyl terminated Al_2O_3 surface with new possible MLD aromatic precursors as hydroquinone bis(2-hydroxyethyl)ether and 1,1′-biphenyl-4,4′- diamine where DFT shows that the selected aromatic molecules react favorably with TMA fragments on the Al_2O_3 surface and are worthy of further experimental investigation.

[1] Arbresha Muriqi, Maarit Karppinen, Michael Nolan, Role of terminal groups in aromatic molecules on the growth of Al_2O_3-based hybrid materials, *Dalton Transactions*, 2021, 50, 17583-17593.

5:15pm **EM3-WeA-16 Engineering Biomimetic Biocompatible and Selectively Antibacterial Ultrathin Films by Vapor Phase Chemistry***, **Karina Ashurbekova**, K. Ashurbekova,* CIC nanoGUNE, Spain*; A. Muriqi,* Tyndall National Institute, University College Cork, Ireland*; L. Barandiaran, B. Alonso-Lerma ,* CIC nanoGUNE, Spain*; I. Šarić ,* University of Rijeka , Croatia*; E. Modin, R. Perez-Jimenez ,* CIC nanoGUNE, Spain*; M. Petravić,* University of Rijeka, Croatia*; M. Nolan,* Tyndall National Institute, University College Cork, Ireland*; M. Knez,* CIC nanoGUNE, Spain

This work describes a strategy for growing conformal ultrathin films of chitin and hybrid chitin-based biomaterials from the gas phase by Molecular Layer Deposition (MLD). We present a new class of organic–inorganic hybrid polymers, which we coin "metallosaccharides", based on sugar monomers as precursors. For a controlled growth, we couple the monosaccharide N-Acetyl-D-mannosamine (ManNAc) with trimethylaluminum (TMA) or Titanium tetraisopropoxide (TTIP) from the vapor phase in repetitive cycles to obtain the respective biomimetic alumochitin or titanochitin thin films. The analysis of the resulting films was done by applying ATR-FTIR, X-ray photoelectron spectroscopy (XPS), Solid-state NMR (ssNMR), High resolution TEM (HRTEM) and Energy dispersive X-Ray spectroscopy (EDXS).

The evaluation of the antimicrobial activity of the alumochitin and titanochitin MLD films against Gram-positive (Staphylococcus aureus, S. aureus) and Gram-negative (Escherichia coli, E.Coli) bacteria was assessed. The attachment of the bacteria and their proliferation on metallochitin-covered glass substrates, were analyzed by confocal microscopy. The results show a great antimicrobial activity of both alumochitin and titanochitin MLD films against gram-positive and gram-negative bacteria, making the films highly interesting for the fabrication of bioactive surfaces.

The biocompatibility of both alumochitin and titanochitin hybrid MLD films was characterized by testing the *in vitro*proliferative behaviors of HEK (Human Embryonic Kidney) 93 human cells cultured on the substrates. We mainly focused on the cell attachment and proliferation. All MLD-coated substrates showed higher cell proliferation than the reference samples, namely uncoated coverslips.

The chemical interactions between the precursors ManNAc and TMA or TTIP, and the probability of the hybrid alumochitin or titanochitin film formation were modeled by density functional theory (DFT) and showed energetically favorablereaction mechanisms.

This project has received funding from the European Union´s Horizon 2020 research and innovation programme under the Marie Sklodowska -Curie grant agreement No 765378.

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