Nanostructure Synthesis and Fabrication
Room Regency Ballroom A-C - Session NS-TuA

Nanostructures and Membranes

Moderators: Christian Dussarat, Air Liquide Laboratories, Michelle Paquette, University of Missouri-Kansas City

4:00pm **NS-TuA-11 Chemical Vapor Functionalization of Polymer Membranes for Water Treatment*, Jeffrey Elam,*** *A. Mane, R. Pathak, R. Shevate, V. Rozyyev,* Argonne National Laboratory

Polymer membranes are used extensively in water purification to filter and remove particulate and molecular contaminants. Ideally, these membranes should exhibit high permeance, selectivity, and fouling resistance, but these attributes are rarely achieved simultaneously. One approach to improve membrane performance is to modify the polymer using reactive chemical vapors to impart the desired physiochemical properties. In this presentation, I will describe recent work at Argonne using atomic layer deposition (ALD), sequential infiltration synthesis (SIS), and vapor-phase grafting to modify polymer membranes used for ultra- and nano-filtration in water treatment. These techniques rely on self-limiting chemical reactions between gaseous precursors and a solid surface to grow material in an atomically controlled fashion. We have used ALD to produce ultrathin and conformal inorganic layers allowing the membrane pore size and pore wall composition to be precisely tuned, SIS for the bulk modification of polymers by creating an organic-inorganic hybrid material, and vapor-phase grafting of small molecules to achieve additional control over the membrane surface properties. Our studies employ a suite of in-situ and in-operando measurements to elucidate the surface chemistry for these processes and extensive ex-situ characterization and testing to understand the effects of chemical vapor treatment on polymers and how they impact membrane performance.

4:15pm **NS-TuA-12 The Molecular Structure of Desalination Polyamides Made by Molecular Layer Deposition*, Brian Welch,*** Technion, Israel*; E. Antonio, T. Chaney, O. McIntee,* University of Colorado at Boulder*; J. Strzalka,* Argonne National Laboratory*; V. Bright, A. Greenberg, M. Toney,* University of Colorado at Boulder*; T. Segal-Peretz,* Technion, Israel*; S. George,* University of Colorado at Boulder

The leading method for creating thin, selective polymer films for desalination membranes is interfacial polymerization (IP). Notwithstanding, IP is challenging to control, and isolated films are difficult to develop and study. Molecular layer deposition (MLD), on the other hand, provides a means to synthesize and study polyamide films, and it serves as a promising direct route for membrane fabrication. This work probes the molecular structure of two prominent desalination polyamides synthesized by spatial MLD. Comparisons between the MLD and IP synthesized films shed light on the role of polyamide molecular structure on membrane performance and on the formation of crosslinked polymers via MLD.

MLD with m-phenylenediamine and trimesoyl chloride produced a crosslinked, aromatic polyamide which is prevalent in commercial reverse osmosis membranes, while MLD of piperazine and trimesoyl chloride formed polypiperazine amide, commonly used in nanofiltration membranes. Growth rates were 2.9 and 1.5 Å per cycle at 115°C, respectively. Grazing-incidence x-ray scattering showed oriented molecular spacing features of 3.8 Å in the reverse osmosis polyamide, and larger, isotropic spacing features of 4.6 Å in the nanofiltration films. These orientation and size differences, rather than the crosslink density, correlate to membrane water passage and solute retention.

From ellipsometry and x-ray reflectivity results, we posit that the surface of crosslinked organic MLD films is comprised of polymer tails up to two monomers in length which are connected to a crosslinked bulk layer. These segments are short in comparison to un-crosslinked MLD chemistries whose long segments experience thermal motion which make double reactions more probable with increasing temperature. The structure and surface of MLD and IP polyamide films were compared using x-ray photoelectron spectroscopy, infrared spectroscopy and atomic force microscopy. The MLD films presented properties which are favorable for salt rejection, water flux and fouling resistance: compared to IP, MLD films were dense, highly crosslinked, smooth and homogenous in molecular structure. These results contribute to understanding MLD behavior as well as the synthesis and performance of reverse osmosis and nanofiltration membranes.

4:30pm **NS-TuA-13 Deposition of an Atomic Layer Inside Microfluidic Channel*, Albert Santoso,*** *J. van Ommen, V. van Steijn, M. David, Y. Hounat, R. Zheng, N. Wijers, J. de Roeck,* TU Delft, Netherlands

Since its introduction in the field of microfluidics in 1998, polydimethylsiloxane (PDMS) has seen a rapid increase in its use as a material to construct microfluidic devices. However, its broad application is limited by the absence of its surface anchoring groups and its incompatibility with common organic solvents. Current strategies to address these shortcomings include altering PDMS throughout leading to unwanted changes to the bulk properties or modifying its surface often leading to relatively thick layers.

We present a novel strategy to deposit an atomic layer of metal oxides (TiO_x and SiO_x) on the inside of PDMS microfluidic channels using atmospheric pressure atomic layer deposition (AP-ALD). We alternatingly flow nitrogen carrier gas convectively containing the precursors (TDMAT, $SiCl_4$, ozone, or water) through the microchannels (aspect ratio of 30-200). Infiltration of the porous PDMS walls results in a unique surface-subsurface layer, providing a robust hydrophilic barrier that prevents swelling of PDMS upon contact with organic solvents (Santoso et al. Chemical Communications, 2022). Additionally, little to no changes are observed in the transparency and mechanical property of PDMS. We then studied the use of this coated channel for various applications such as isotope extraction involving common organic solvents. Using the coated chip, we managed to extract 98%±2% natural Ga isotope. As a comparison, the non-coated microfluidic chip leaked and it was difficult to even establish a fluid flow. Using the same set-up, we also deposited TiOx – gold nanoparticle and performed photocatalytic Rhodamine B dye reduction. After 1 minute of contact time, we achieved 30% reduction with comparable kinetic behaviour with previously reported value (Hashemi et.al., Nanoscale, 2020). This study demonstrates ALD as a tool to broaden the application of PDMS devices. This enables the use of PDMS microfluidic system in various high-end applications, positively contributing to the emerging fields involving precision and better contact area such as bioassays and photo-based micro-reaction.

4:45pm **NS-TuA-14 Tunable and Scalable Synthesis of ZnO Nanostructures using ALD Seed Layers*, Alondra M. Ortiz-Ortiz*,** *A. Gayle, J. Wang, D. Delgado, D. Penley, H. Faustyn, K. Fuelling,* University of Michigan, Ann Arbor*; A. Bielinski,* Argonne National Laboratory*; C. Sherwood, N. Dasgupta,* University of Michigan, Ann Arbor

There has been significant advancement in the synthesis of nanostructured materials for use in biological, environmental, and energy fields in recent decades, with many novel processes demonstrated at the laboratory scale. Nevertheless, challenges remain at the nanomanufacturing frontier, where it is necessary to maintain tunable material structure and properties using high-volume, high-throughput, and low-cost processes. One of the most facile techniques for the tunable and scalable synthesis of nanostructured materials is atmospheric-pressure hydrothermal synthesis of ZnO, which occurs under mild conditions. We have previously demonstrated that by using Atomic Layer Deposition (ALD) to deposit tunable "seed layers" with sub-monolayer precision in composition and structure, we can programmably tune geometric parameters (spacing, length) of the resulting ZnO nanostructures [1]. We refer to this process as "surface directed assembly", which has been used to enable applications ranging from photocatalysis to anti-biofouling surfaces [2,3].

In this study, we explore a third dimension of programmable control: using ALD seed layers to tune the ZnO nanostructure shape. Specifically, we demonstrate synthesis of Al-Zn-O nanosheets (NSs) using the surface directed assembly process by depositing a seed layer of Al_2O_3. The formation of a zinc-aluminum layered double hydroxide phase occurs from the interactions between the Al and Zn^{2+} ions during the hydrothermal synthesis, as confirmed by X-ray Diffraction (XRD). We demonstrate that the density of the ZnO NSs can be controlled by the number of cycles of Al_2O_3. Furthermore, Scanning Electron Microscopy (SEM) analysis shows that a transition from NS to nanowires (NWs) occurs after extended growth time. To rationalize this behavior, we propose a "phase diagram" for surface directed assembly of nanostructures using ALD. Additionally, we demonstrate the ability to scale-up this surface-directed assembly process onto non-planar, large (cm-scale) surfaces facilitated by the design of a customized flow reactor. This work provides a new pathway to scalable nanomanufacturing enabled by the precise interfacial tunability of ALD for macroscopic applications, including medical devices and marine sensors.

References:

[1] A.R. Bielinski, M. Boban, Y. He, E. Kazyak, D.H. Lee, C. Wang, A. Tuteja, N.P. Dasgupta, *ACS Nano* **11**, 478 (2017).

[2] J. Wang, S. Lee, A.R. Bielinski, K.A. Meyer, A. Dhyani, A.M. Ortiz-Ortiz, A. Tuteja, N.P. Dasgupta, *Adv. Mater. Interfaces* 2000672 (2020).

[3] A.R. Bielinski, A.J. Gayle, S. Lee, N.P. Dasgupta, *ACS Appl. Mater. Interfaces* **13,** 44,52063–52072 (2021).

5:00pm **NS-TuA-15 Block Copolymer Templated HfOx Nanowires – From Fundamental Understanding to Rational Design***, **Ruoke Cai,** T. Segal-peretz,* Technion, Israel

Hafnium oxide (HfO_2) is an attractive material for optoelectronic applications and high-κ dielectrics in semiconductor devices due to its advantageous properties- high dielectric constant, wide band gap, and high stability. However, hafnium oxide nanostructure fabrication currently relies on complex nanofabrication processes. Sequential infiltration synthesis (SIS)- a method derived from atomic layer deposition (ALD), in which vapor phase precursors diffuse into polymers and react with them to form hybrid material, can provide a simple and cost-effective alternative for these processes.

In this study, we demonstrated the formation of hafnium oxide nanostructures- vertical and horizontal nanowires,usingblock copolymers (BCPs) templates. BCPs were self-assembled into highly ordered and periodic nanostructures, followed by hafnium oxide SIS process. In SIS, selective interactions between the hafnium organometallic precursor and the polar block of the BCP resulted in selective growth within the polar block domains. Following the growth, the BCP template was removed to yield hafnium nanowirestemplated by the BCP morphology. We first explored the precursor-polymer interactions in various homopolymers using *in-situ*quartz crystal microbalance (QCM) microgravimetric measurements. This fundamental understanding was further applied in finding a suitable BCP for templating HfO_2 inorganic nanostructure. We probed the formation of vertical and horizontal nanowires from the BCP templates using high-resolution TEM, EDS, and XPS. This research demonstrates the rational design of the HfO_2 nanostructure via template morphology tuning and control over HfO_2 growth.

5:15pm **NS-TuA-16 Compressible Polymer Sponge Electrodes via oMLD of PEDOT onto Polyurethane Sponge Supports***, **Mahya Mehregan,** G. Luebbert, K. Brathwaite, Q. Wyatt, E. Throm, D. Stalla, M. Young,* University of Missouri

The formation of compressible porous sponge electrodes is appealing to overcome liquid phase diffusion limitations in applications including electrochemical energy storage, electrochemical water desalination, and electrocatalysis. Previous work has employed wet chemical synthesis to deliver conductive materials into porous polymer sponge supports, but these approaches struggle to produce functional electrodes due to (1) poor electrical connectivity of the conductive network and (2) mechanical rigidity of the foam after coating. In this work we employ oxidative molecular layer deposition (oMLD) via sequential gas-phase exposures of 3,4 ethylenedioxythiophene (EDOT) and molybdenum pentachloride ($MoCl_5$) oxidant to imbibe polyurethane sponges with electrically-conductive and redox-active poly(3,4 ethylenedioxythiophene) (PEDOT) coatings. We analyze the oMLD deposition on compressive polyurethane sponges and modify the reaction conditions to obtain mechanically compressible and electrically conductive sponges. We specifically identify the importance $MoCl_5$ dose time to enhance the conductivity of the sponges and the importance of EDOT purge time to preserve the mechanical properties of the sponges. This approach produces an electrically conductive PEDOT network within the sponge support with minimal impact on the sponge's mechanical properties, offering advantages over wet-chemical synthesis approaches. The compressible, conductive sponges we generate have the potential to be used as compressible electrodes for water desalination, energy storage, and electrocatalysis.

5:30pm **NS-TuA-17 Low Cost, Large Area Sers Substrates by All Ald Deposited 3d Porous Filter Papers***, **Feng Niu,*** Raytum Photonics

Surface enhanced Raman scattering (SERS) has emerged as a promising spectroscopic tool for ultrasensitive trace detection of target molecules in the vicinity of nanostructured noble metal surfaces. Researchers have developed many techniques to create SERS substrates with most of them falling into three categories: metal nanoparticles by colloidal chemistry, nano-patterned surfaces, physical and chemical vapor deposition or a combination of them. However, all these techniques have limitations to coating hotspots directly inside 3D SERS substrates. On one hand there is high demand for super-enhancement, and ultra-sensitivity SERS substrates, on the other hand it is still challenging due to lack of stability, reproducibility, and reusability for such SERS active substrates to enter the realms of real, practical applications. Thus, new concepts, new techniques for simple, larger area, cost-effective fabrication techniques for SERS substrates are still in demand. Atomic layer deposition (ALD) has shown great performance in various fields such as semiconductor development, catalysis, energy and environmental applications. Due to its unique characteristics of super conformity, large area uniformity, easy layer thickness/composition control with precision in atomic scale, low cost and easy scale-up, if designed rationally it is an excellent technique for the bottom-up fabrication of nano-scaled materials and devices. Thus since 2010 ALD has also been investigated for the fabrication of SERS active substrates including Au or Ag nanoparticles (NP), ultra-thin films, conformal coatings of 3D scaffolds, high aspect ratio nanostructures, core-shell nanostructures, tunable nanogaps and high-density hot spots on nanostructured scaffold, etc.

We successfully developed ALD process for making Ag nanoparticles on 3D porous glass fiber filter paper and investigated evolution of Ag NPs with some key process parameters. By fine tuning Ag nanostructures and controlling cycle numbers we were able to obtain high density isolated Ag NPs without formation of agglomerates and continuous Ag films. We demonstrated the presence of strong localized surface plasmon resonance (LSPR) peaks and discovered multiple LSPR peaks associated with multiple scale NP size distributions. We also demonstrated the presence of the SERS signals on these ALD Ag coated glass fiber filter substrates using pyridine as the test analyte. Our results demonstrate that ALD is not only a very promising technique for the rational design as compared to other existing techniques but also has great potential for the fabrication of large area, low-cost nanostructured substrates for commercial applications.

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