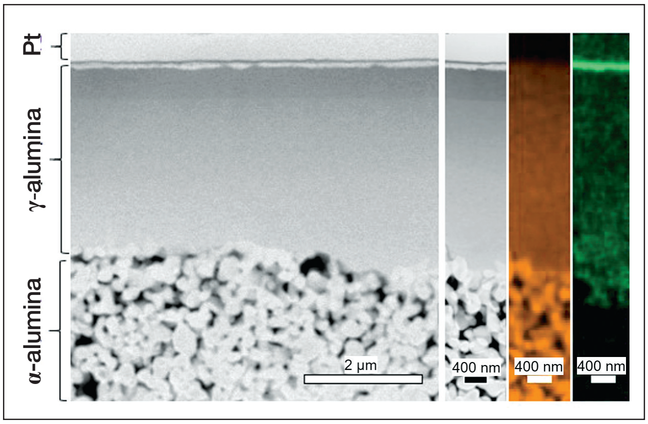
Atomic layer deposition yields highly selective filtration membranes

Filtration technology is essential for many industrial processes. In particular, oil refinery systems must effectively separate paraffins (such as propane) from olefins (such as propylene) in order to conserve and recover the latter, more precious commodity. To date, most large-scale endeavors have relied on distillation to split these organic molecules. These approaches are expensive and energy-intensive. Membrane-based separations, when combined with distillation, can more effectively separate hydrocarbons than conventional distillation-only industrial systems. A metal–organic framework (MOF) called ZIF-8 (zeolitic imidazolate framework-8), when made into a thin membrane film on a support structure, has been found to effectively separate propylene. The biggest hurdle to implementing this hybrid membrane-distillation process is cost: solution-based solvothermal methods used to form these membranes are difficult and expensive to scale up. An all-vapor membrane synthesis method can eliminate the complexities of a liquid- or gel-based processing approach and is much more attractive. However, existing vapor-based atomic layer deposition (ALD) methods have yet to demonstrate converting precursor components into comprehensive, fully functional membranes.

Now researchers from the University of Minnesota (UMN) have adjusted the synthesis method of the zeolitic imidazolate framework to comprehensively reconstruct the selectively permeable membrane and yield a more industrially scalable method that can be used to separate paraffins from olefins. Xiaoli Ma, Michael Tsapatsis, and their colleagues from UMN's Department of Chemical Engineering and Materials Science deposited the sieving materials within a porous substrate. Key to their efforts was a two-step vapor-based process that first used ALD with diethyl zinc water vapor to deposit ZnO into a layer of mesoporous γ-alumina on a macroporous α-alumina support. They then transformed the ZnO into a MOF by exposing it to 2-methylimidazole (a volatile organic molecule) in a ligand-induced permselectivation (LIPS) process.



Microstructure of the manufactured membrane is revealed through (left to right) cross-sectional analysis, annular dark-field scanning transmission electron microscopy, and spatial distribution of aluminum (orange) and zinc (green) for the ZIF-8 nanocomposite membrane. Credit: Xiaoli Ma.

The resulting selectivity of propylene over propane was larger than 50, and the propylene flux was high enough to be commercially attractive. The researchers published their approach to capture the propylene olefin in a recent issue of *Science* (doi:10.1126/science.aat4123).

"By looking at the cross section of the membrane at different stages of fabrication using focused ion beam milling and scanning transmission electron microscopy, we were able to study the penetration of zinc oxide into the porous alumina support at the nanoscale," says Prashant Kumar, a member of the research team. "This allowed us to tune our ALD method for optimal membrane performance," he added.

The resulting membranes yielded significantly higher propane/propylene selectivity than comparable zinc-based MOFs that were reported in the past. In addition to being more industrially scalable than conventional solvothermal methods, the combination of an ALD step followed by a LIPS eliminates nonselective gaps, such as pinholes and grain boundaries, in the resulting membranes. The approach by Ma, Tsapatsis, and their UMN colleagues stands to aptly compete with conventional molecular sieving methods in a broad range of industrial and laboratory applications.

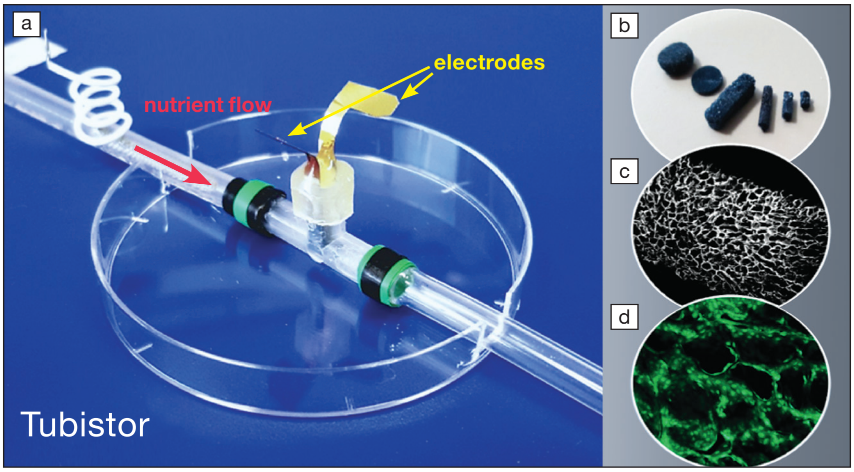
Boris Dyatkin

Bio Focus

3D tubular platform monitors cell cultures

Organ-on-chip platforms are fluidic systems used to monitor the response of a large variety of cell types to drugs and external stimuli in real time. These platforms typically use flat electrodes made of electrically conductive polymers, and the growth and evolution of cell cultures is followed through modulations of the electrical conductivity with time. However, two-dimensional (2D) platforms cannot fully capture the *in vivo* physiology of three-dimensional (3D) tissues and could result in misleading outcomes. In this context, in a study published in a recent issue of *Science Advances* (doi:10.1126/sciadv.aat4253), an international collaborative team led by Róisín Owens from the University of Cambridge reports the development of a 3D tubular strategy to host and monitor growth of cells in 3D.

In this work, a commonly used biocompatible and electrically conductive polymer, PEDOT:PSS, was freeze-dried to create a porous scaffold to support the cells' invasion. This conducting porous scaffold can be created directly *in situ* inside a tube or prefabricated, then inserted into a T-shaped tube, called a "tubistor" (see Figure). This represents



(a) Three-dimensional T-shaped tubistor in an 8-cm-diameter petri dish, with (b) the electrically conductive porous scaffold placed inside, (c) its microstructure, and (d) with green fluorescent cells. Image courtesy of Róisín Owens.

a 3D transistor that is connected to fluidic tubes to allow a linear flow of the liquid containing the cells, and to three electrodes. The device functions as a transistor and will amplify electrical signals recorded during the experiments. This geometry is particularly interesting, as it can mimic native blood vessels, soft tissues, and even organs.

The researchers tested the device using model mammalian cell lines that were fluorescently labeled. The conductive porous scaffolds were perfused by a continuous flow of cell medium, and the current in the transistor was recorded with time. At the same time, the morphology and number of the cells was monitored by fluorescence microscopy to determine the origin of the changes in electrical conductivity. The researchers observed that after cell seeding, their attachment and growth in the device led to a significant decrease in the conductivity. After two days, the electrical response stabilized, demonstrating that a steady state had been reached. “In the future, we hope to have a system that will monitor longer term effects, such as a week,” says Charalampos Pitsalidis, the first author of the article.

The team plans to use the tubistor for continuous toxicology monitoring. Preliminary data using a drug that bound to calcium have already shown that cells were affected after only 15 minutes. In the future, Owens’s team will perform electrical stimulation experiments with various cell types, including electroactive cells, and study the effect of various compounds on the fully formed tissues.

Lesley Chow, assistant professor in bioengineering at Lehigh University and who did not take part in the study, explains that “culturing cells in 3D is necessary to mimic the extracellular microenvironment found in native tissues. The authors demonstrate that advances in bioelectronics can be exploited to help us learn more about how cells respond to their microenvironment in real time. This is likely to have a major impact on tissue engineering, as such 3D devices will accelerate the optimization of biomaterials design.”

Hortense Le Ferrand

Nano Focus

MXenes poised to improve wearable artificial kidney options

Atomically thin two-dimensional (2D) materials are a burgeoning class of structures that now encompass numerous chemistries beyond graphene. They offer highly versatile properties and promising capabilities that transcend the limits of traditional materials. While certain obvious applications immediately jump to mind for these materials—electronics, memory chips, and energy storage—novel biomaterials also stand to benefit from 2D nanostructures. In particular, wearable artificial kidneys, which conduct round-the-clock dialysis for patients with end-stage renal failure, require new sorbents in order to become sufficiently lightweight, portable, and efficient to provide this lifesaving treatment.

In order for wearable kidneys to efficiently function, they must regularly remove urea molecules from the dialysate solution, which constantly collects these toxic molecules out of blood during dialysis. Traditional methods require catalytic decomposition and outgassing of carbon dioxide and adsorption of ammonia, another decomposition product. This solution is not acceptable and will not work for a proper wearable medical device. On the other hand, 2D materials can effectively trap urea molecules between their atomically thin sheets—but only if the surface chemistry, as well as the interatomic spacing of the laminates, is properly tailored for this process.

A relatively new class of 2D transition-metal carbides and nitrides, called MXenes, appears well-suited for this task. The atomically thin delaminated layers of MXenes are composed of metals (such as titanium) bonded to carbon and/or nitrogen, and terminated with oxygen, hydroxide, or fluoride surface groups. They resemble clays and can accommodate molecules such as water and urea. A team of materials researchers from Drexel University, alongside visiting scientists from Guangxi Medical University and Huazhong University of Science & Technology, and collaborators from Cedars-Sinai Medical Center and the University of Brighton, used this MXene material to remove almost all dissolved urea from dialysate solutions and to absorb 22 mg of this waste material per gram of sorbent. The researchers published their breakthrough in a recent edition of *ACS Nano* (doi:10.1021/acsnano.8b06494).