AIChE JOURNAL Highlight

Challenges and Opportunities in Layer-by-Layer Assembly

Layer-by-layer (LbL) adsorption is a technique used to incorporate a range of different materials using alternating electrostatic charge to form multilayered films. This process enables the engineer to control film composition with molecular and nanoscale precision — a key requirement for applications ranging from drug delivery to sensing devices.

In the November *AIChE Journal* Perspective article, "Engineering Materials Layer-by-Layer: Challenges and Opportunities in Multilayer Assembly," Massachusetts Institute of Technology professor of chemical engineering Paula Hammond discusses the state of LbL technology and explores some of the applications where it will likely prosper.

Layer-by-layer technology offers several advantages as a way to create multilayered films. One of the most important is the ability to combine polymers, small molecules, and inorganic materials in a single thin film without some of the constraints typically associated with such blends. The adsorbed layers of a polyelectrolyte multilayer film are highly interpenetrated, so polymer chain segments in one layer will likely exist in several layers below and above the point of adsorption. This property is especially important in the design of membranes that regulate the transport of ionic, electronic, and molecular species.

While this highly penetrating nature of polymer chains enables molecular-level blending, on a larger scale, discrete regions of homogeneous composition can be created with LbL assembly — allowing the engineer to control material structure at the nanoscale. This is of particular interest for controlled-release drug delivery.

"Multilayer assemblies offer the unique advantage of introducing a range of different types of drugs into the thin film. If one can generate films in which release is based predominately on surface erosion, it should be possible to incorporate different drug components at different layers in an LbL film. This film would then erode to release the drugs in the inverse sequence of their construction," Hammond says.

Another benefit of LbL assembly is that it can be used to form "novel composite structures with compositions and morphologies that would be difficult to achieve through direct mixing or blending of traditional polymers," Hammond says. Because LbL uses a charged nanomaterial that is fully dispersed in water and is self-stabilizing, it does not form aggregates, as is typical of organic solvent-based dispersions. Thus, the nanomaterial exists within the multilayer film as an individual entity with highly accessible surface area — making it possible to achieve improved percolative properties at low nanomaterial concentrations.

▲ In this automated LbL setup, nozzles spray separate streams of both positively and negatively charged species, as well as a rinse stream used between each adsorption step. Image courtesy of MIT Press.

Hammond describes an example of a film made by depositing (via LbL) alternating layers of positively and negatively charged carbon nanotubes (CNTs). Unlike cast films, in which the nanotubes form bundled aggregates, the LbL film consists of well-isolated nanotubes — resulting in a high density of nanotubes plus a large amount of available surface area created by the open network of the CNTs.

Before LbL technology can move beyond demonstrations to real-world applications, several challenges must be addressed, Hammond acknowledges. The most significant of these is developing the ability to produce the thin films at sufficiently high throughput and low cost, she says. While the traditional dipping process with slight variations offers a suitable process for simple thin films, other methods must be devised for thicker, more-complex systems.

Over the past 10–15 years, several promising methods have been investigated. For example, the feasibility of spraying alternating polyelectrolyte solutions onto a substrate has been demonstrated. Hammond and her colleagues recently developed the first automated spray-LbL process with cycle times on the order of tens of seconds rather than the 30–45-min cycles typical of conventional systems.

"The reduced cycle times, combined with the ability to adapt the nozzle spray structure, change the number of nozzles, and control the arrangement of the substrate, yield a versatile and highly efficient system for manufacturing thin multilayered film coatings. Ultimately, the use of roll-to-roll manufacture, implementation of sophisticated rapid-spray technologies, and use of existing manufacturing infrastructure for spray-coating applications will make the generation of these films highly accessible to industry. It is anticipated that spray-LbL will be one of the primary means by which this approach will lead to commercial technologies," Hammond says.

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