Nanomembranes

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Converting Molecular Monolayers into Functional Membranes

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2D films · cross-linking · monolayers · nanomembranes · nanosheets

Nanomembranes are extremely thin (< 5–10 nm), synthetic two-dimensional (2D) layers or sheets with tailored physical, chemical, or biological functions. With their two opposing surfaces, they interface and link different environments through their distinct physical and chemical properties, which depend on their thickness, molecular composition, and structure and the environment on either side. Due to their minute nanometer thickness and 2D architecture, they can be regarded as "surfaces without bulk" separating regions with different gaseous, liquid, or solid components and controlling any materials exchange between them.

The translocation of molecules, ions, or electrons through membranes is a key process in living and in technical systems. In biology, lipid bilayers with embedded highly specialized proteins separate the interior of organelles and cells from the outside world and regulate all transport in and out. In technical systems, organic and inorganic membranes can also act as barriers or filters. However, for many technologically relevant translocation processes no functional membranes are available, and material separation is realized by energy-wasting procedures such as distillation, centrifugation, and electrophoresis. To make things even worse, the permeation through conventional technical membranes is characterized by spatially confined diffusion through one-dimensional channels that force particles into a single file with a fixed spatial sequence (Figure 1 A). This severely restricts the possibility for large displacements and effective permeation rates. Conversely, nanomembranes allow a quick passage through the pores—like sand through a sieve—resulting in high throughput at low energy input. Nanomembranes thus provide inherently the basis for a low-cost, energy-efficient green technology.[1] This also holds for nanofluidic devices and biomimetic applications that require specialized and miniature nanopores to allow the passage of long chain-like macromolecules like DNA, which must uncoil and disentangle before it is inserted and translocated (Figure 1 B). The creation of innovative types of nanomembranes, the investigation of their structural and functional properties, and the exploration of their performance in filtration, separation, sensing, analysis and sequencing are thus desiderata.

In the 1930s Langmuir and Blodgett assembled amphiphilic molecules on water surfaces to form membrane-like structures that were then transferred onto solid surfaces.[2] For decades, these Langmuir–Blodgett (LB) films were investigated as ultrathin reference systems and utilized for the functionalization of surfaces with organic moieties. In the 1980s, Sagiv, Nuzzo, and Allara introduced self-assembled monolayers (SAMs),[3] that is, monomolecular films formed by the spatially controlled organization of molecules on solid surfaces. SAMs have been investigated in great detail and provide a straightforward approach to coat and functionalize solid surfaces with molecule-thick nanolayers. In the 1990s the so-called layer-by-layer (LbL) technique[4] was introduced by Decher to fabricate membranes for corrosion protection, sensing, and drug delivery. In the LbL process, an electrically charged surface is sequentially dipped into positively and negatively charged polyelectrolytes, leading to the formation of polymeric membranes of well-defined molecular composition with thicknesses from roughly 15 nm to several hundred nanometers. In the 2000s, Geim and Novoselov introduced graphene,[5a] a carbon nanomembrane with the thickness of only one atom; it received a lot of attention, as it opened fascinating insights into novel 2D systems, which was acknowledged with the 2010 Nobel Prize in Physics. Nowadays, graphene is also investigated as a filtration membrane

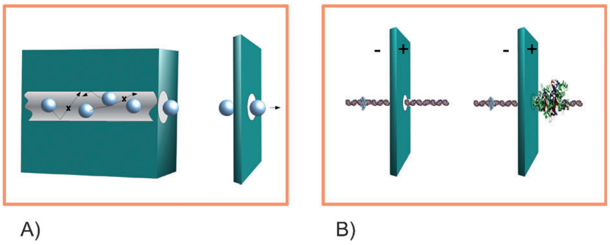

Figure 1. A) If a channel has almost the same size as the particle, single-file diffusion reduces throughput. In nanosheets, the channel length is comparable to the particle diameter. B) Molecular translocation of long-chain molecules through nanopores is governed by unfolding dynamics.

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where translocation of molecules occurs through lithographically produced pores.[5b] However, as perfect graphene is homogeneous and chemically inert, it is not well suited for surface functionalization. Hence, there remains a great need for the development of ultrathin free-standing membranes with tailored, chemically active surfaces. Along this path, chemists and physicists work together on innovative strategies to build and to explore novel types of 2D materials, engineered nanolayers, and artificial membranes.

A powerful scheme to fabricate carbon nanomembranes (CNMs) starts with the generation of a functional molecular monolayer on a solid surface. In the next step, this layer is cross-linked to form a molecularly thin membrane that can then be released from the surface. As this CNM inherits its thickness, surface functionality, and defects from the original molecular layer, nanosheets with well-defined properties can be tailored.[6] CNMs have been made from a variety of aromatic self-assembled monolayers, combining the thickness and mechanical stability of graphene with the chemical functionality of a SAM. The mechanical, optical, and electrical properties of CNMs are thus to a large extent determined by the initial molecular monolayer.

In recent and related work, Frauenrath et al.[7] constructed carbon nanosheets from amphiphilic hexayne monolayers on a water surface. The molecules were assembled in a Langmuir–Blodgett trough that allowed the compression of the floating film into different molecular packings. The authors showed that the molecules form well-ordered films and preferably assembled in an all-*trans* configuration, as seen in Figure 2. The molecular films are then cross-linked to form mechanically stable nanosheets by exposure to UV irradiation (Figure 3). Note that the cross-linking affects only the acetylene groups in the central section of the molecule and that the number of linkages is determined by the radiation dose as well as by the number of acetylene groups and their molecular packing. Hence, by varying the type of molecules, the surface area, and the exposure conditions, it is possible to tailor the mechanical properties, that is, stiffness, thickness, and permeability. Finally, Frauenrath et al. showed that their nanosheets can be transferred onto other solid supports where they can be further investigated by IR, UV/Vis, and Raman spectroscopy and imaged by transmission electron microscopy.

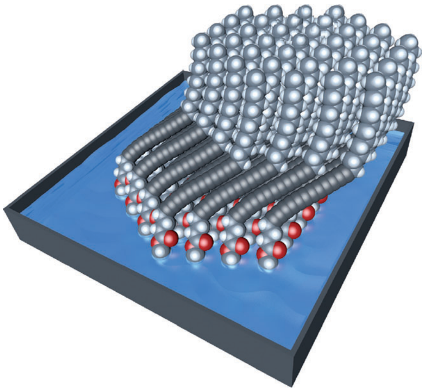

Figure 2. Well-ordered monolayer of amphiphilic hexayne at the air/water interface. Adapted from Ref. [7].

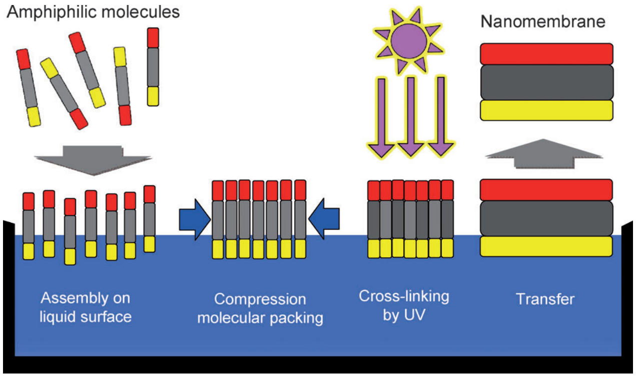

Figure 3. Nanomembrane fabrication starting from amphiphilic molecular precursors on a liquid surface.

Building on earlier efforts, the fabrication scheme by Frauenrath et al. offers more flexibility and practical advantages, which will bring nanomembranes closer to applications in filtration. Firstly, the preparation of monolayers on liquid surfaces is possible with a wide variety of molecular precursors. Recently, a lot of activity in the preparation of covalently[8] and organometallically[9] linked 2D polymers has been reported, and as this field is growing, more molecular 2D systems, for example peptoid-based[10] monolayers are being constructed. Secondly, the preparation at the liquid–gas interface in an LB trough further offers the possibility of affecting the molecular packing by controlling the surface area and surface stress. This is not feasible on solid surfaces, and may become an advantage in the search for the best steric conditions for optimal cross-linking. In the long term, it will be interesting to see whether the tedious LB technology will lead to a relatively simple and efficient approach for scaling up nanomembrane production, with the benefit of the simple and direct transfer of the resulting nanomembrane from a liquid onto another surface. In general, it is expected that stacked nanomembranes—sometimes termed as van der Waals heterostructures—would be perfect building blocks for novel types of functional (hybrid) systems. When incorporated into devices, they should allow a further fine-tuning of mechanical, electrical, optical, and translocation properties. Driven by these applications, the described research is another important step to a 2D materials chemistry from which we expect further growth and fascinating applications in the near future.

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