

# SURFACE MODIFICATION FOR ENHANCING MEMBRANE QUALITY

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## Surface Modification

Surface modification of existing polymeric membranes has become a pivotal aspect of membrane science, aiming to improve membrane performance and introduce novel functionalities. These modifications focus on altering the surface properties without changing the membrane's bulk structure. Different methods are employed for this purpose, such as coating, self-assembly, surface graft polymerization, and the sol-gel technique.

### Coating Method:

Through on-site synthesis of a polymer or by coating the membrane with another polymer, it's feasible to create layers affixed to the membrane material via diverse mechanisms. These mechanisms involve adsorption/adhesion, where the functional layer is physically attached to the base material. Strengthening these bonds can occur through multiple interactions between functional groups within the macromolecular layer and the solid surface. Another mechanism is interpenetration, resulting from the mixture between the added functional polymer and the base polymer in an interphase. Additionally, mechanical interpenetration occurs between an added polymer layer and the pore structure of the membrane.

Coating these functional materials onto the membrane can profoundly alter its surface properties, transitioning from hydrophobic or non-biocompatible to hydrophilic and biocompatible. However, this method might not offer a stable surface for materials absorbed on the membrane surface, as they can easily displace.

One of the most critical surface coating modifications on a technical scale involves in situ crosslinking copolymerization of hydrophilic acrylate monomers within macroporous membranes made from hydrophobic materials like polypropylene or poly(vinylidene fluoride). This reaction results in a durable hydrophilic layer on the pore surface, achieved through a thin polymer layer. While the possibility of coupling to the surface via radical reactions exists, the primary mechanism for fixation remains the mechanical interpenetration between the added polymer network and the base membrane's pore structure. These surface-modified membranes are commercially available materials and serve as the foundation for the development of innovative products such as membrane adsorbers. This advancement showcases the potential to revolutionize membrane technology for broader industrial applications.

## Self-Assembly Technique:

Self-assembly, a commonplace occurrence in nature, plays a pivotal role in membrane surface engineering, involving the formation of self-assembled monolayers and layer-by-layer assembly. This process is initiated by the adsorption of an active surfactant onto a solid surface, leading to the creation of ordered molecular assemblies. The two-dimensional systems' organization is a result of chemical synthesis at the interface, eventually reaching equilibrium.

In 1991, Decher and collaborators introduced a film assembly method utilizing alternate adsorption of linear polycations and polyanions, or bipolar amphiphiles. This technique involves excessive adsorption at each stage of the polycation/polyanion assembly, rejuvenating the outermost surface during each step of film formation. Its applicability in membrane surface functionalization stems from its simplicity and adaptability. Notably, this process boasts several advantages over alternative techniques. It relies on spontaneous adsorption, eliminating the need for stoichiometric control to maintain surface functionality. The resultant molecular layers exhibit increased thermal and mechanical stability. An exceptional advantage lies in its versatility, not limited to a specific substratum, allowing nanoscale-level surface design.

Layer-by-layer adsorption of polyelectrolytes presents a relatively novel coating method rooted in supramolecular assembly. This technique offers the distinctive feature of vertical organization and stabilization of layers, enabling the design of both outer surface and internal layer structures across diverse base materials. While these multilayers might not achieve perfect order, the building principle compensates for defects in surface coverage at minimal total layer thickness. These attributes contribute significantly to the robustness of the coating technology and the resulting layers, ensuring their stability under various application conditions.

For the successful implementation of the layer-by-layer technology, the membrane should exhibit the ability to adsorb the initial polyelectrolyte layer via ionic bonds. However, the surface doesn't necessitate an extremely high density of charged functional groups. Membranes suitable for this technique encompass plasma-treated polyacrylonitrile ultrafiltration membranes, surface-modified polypropylene membranes, or anopore membranes derived from aluminum oxide.

## Graft Polymerization:

Surface graft polymerization is a process wherein macromolecular chains are bonded covalently to a membrane surface, offering a unique advantage of tailoring the membrane to possess distinct properties. The choice of different grafting monomers facilitates the customization of the membrane surface while retaining its fundamental properties. This technique allows for the precise introduction of chains onto the membrane surface with high density and exact localization, ensuring a controlled modification. Unlike physical modification methods like coating, covalently attaching polymer chains prevents desorption and ensures the long-term chemical stability of the modified surface.

Grafting methods generally fall into two categories: "grafting-to" and "grafting-from." In "grafting-to," preformed polymer chains carrying reactive groups are coupled covalently onto the membrane surface, providing controlled synthesis and detailed characterization of the modifying polymer. However, it has limitations in surface grafting densities and often demands specialized coupling reactions. Conversely, "grafting-from" methods, although less controlled regarding polymer structure, offer versatility in obtaining varying grafting densities and chain lengths under more convenient reaction conditions.

Various strategies have been explored to introduce macromolecular functional layers onto membrane surfaces:

- Direct coupling on reactive groups of the membrane material, like cellulose derivatives, polyamides, or polysulfones.
- Primary functionalization of the membrane by introducing amino, aldehyde, epoxide, carboxyl, or other reactive groups on the surface followed by subsequent coupling.
- Adsorption on the membrane surface followed by physically activated coupling, such as nonselective fixation via plasma treatment or selective UV irradiation, enabling versatile modifications

"Grafting-to" reactions have been effectively utilized to functionalize membranes, particularly ultrafiltration or microfiltration membranes, with hydrophilic macromolecules or other functional polymers to regulate interactions with the membrane surface. This includes minimizing protein adsorption, binding metal ions, or covalently coupling ligands to the surface.

For synthesizing macromolecular layers via "grafting-from," radical polymerization reactions using a variety of functional monomers have been extensively employed. Physical activation techniques such as electron beam, plasma treatment, or direct UV excitation have been explored to create radicals and initiate polymerization. However, limitations arise from changes in membrane morphology and uneven modifications within porous membranes.

Chemical grafting involves activating functional groups on the membrane surface and reacting them with monomers or macromolecules. The grafting process, either free radical or ionic, depends on the type of initiator species. Recent advancements in living polymerization methods hold promise by providing regulated molecular weights and controlled, uniform polymer layers on membrane surfaces.

