Chemoselective Nanoporous Membranes Formed by Scalable Self-Assembly of Random Copolymer Micelles

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Membranes that can separate compounds based on molecular properties can revolutionize the chemical and pharmaceutical industries. However, finding a simple and scalable approach which confers the membrane with high permeability, selectivity, and systematic tunability is still an unmet challenge, especially when the molecules to be separated are small. Integration of chemical functionalities into membrane nanopores requires engineering the pores and functionalizing them with specific groups to induce desired chemical interactions with the target molecule. The key to design such membranes with superior selectivity and permeability is confining the flow of solute to a small channel size (comparable to solute size) of about 1-3 nm as well as incorporating high density of functional groups just like biological pores.

Inspired by these biological pores, we designed a novel and simple approach to create such chemoselective membranes for separation of sub-nanometer size molecules. We synthesized an amphiphilic random copolymer that combines highly hydrophobic, fluorinated repeat units of 2,2,2-trifluroethyl methacrylate (TFEMA) with charged, hydophilic units of methacrylic acid (MAA), PTFEMA-*r*-PMAA, by free radical polymerization, a simple, robust and scalable synthesis method. The high incompatibility between the two segments led to spontaneous formation of spherical micelles in solution of alcohol with carboxylic acid groups on the micelle corona. The membrane is then manufactured using the self-assembly of these micelles by a simple and scalable coating process on a commercial porous support. The interstices between these packed array of micelles serves as charged nanochannels (1-3nm) through which water and solutes can pass. The high density of negatively charged carboxylate groups along the pores lead to high separation selectivities between sub-nanometer organic solutes of similar size but different charge. In single solute diffusion experiments, neutral solutes permeate up to 263 times faster than negatively charged compounds of similar size. Similar to biological pores, this selectivity is enhanced significantly in experiments with mixtures of these solutes. No permeation of the anionic compound was observed for over 24 hours. In filtration experiments, these membranes separate anionic and neutral organic compounds while exhibiting water fluxes comparable with commercial membranes.

Furthermore, carboxylate groups can be easily converted to other functionalities using a straightforward conjugation chemistry. When the carboxylate groups were replaced by selected functional groups, the membranes showed an unprecedented selectivity up to 12 for two small organic molecules of identical size and charge based on their chemical structure. This further demonstrates these membranes are easily customizable, which enables a broad range of selective separations. This is the first demonstration of a new approach to forming membrane selective layers by micelle self-assembly of easily synthesized random copolymers. The approach is easily adaptable to address various pore sizes and pore surface chemistries, leading to novel membranes with high permeability and selectivity.