



Engineering hybrid ceramic membranes through innovative grafting approaches

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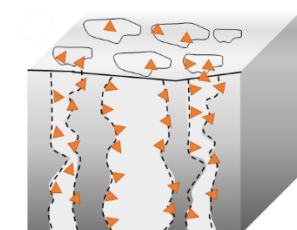
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Surface modification of micro/mesoporous ceramic membranes by covalent attachment of molecules, short polymer chains or polymeric networks provides the opportunity to prepare hybrid systems with controllable pore surface properties. Such control offers the possibility to design hybrid ceramic-based membranes in the NF or UF range which can be used for example for the recovery of dyes [1], or separation of biomass mixtures [[2]]. These hybrid membranes are prepared using pre-synthesized molecules or polymer brushes composed of a reactive linking group able to react with the surface group of the mesoporous ceramic membranes [3]. Especially the phosphonic-acids-based linking groups were shown suitable for preparing hybrid membranes by grafting [[4]]. However, with the common solution phase grafting method, limited grafting yields are obtained due to inaccessible surface sites (i.e. hydroxyl groups, acidic sites) blocked by the first grafted or physisorbed polymer brushes or molecules at the ceramic membrane pore surface. As a consequence, these unoccupied surface sites can bias the separation performance of e.g. dye molecules due to unwanted adsorption on the non-reacted -OH sites of the oxide ceramic membrane.

To overcome this diffusion limitation of phosphonic acid-based polymer brushes during grafting, we present here, a set of novel grafting methods to confine polymer brushes into mesoporous ceramic membranes. Pore size measurements and membrane performance tests are shown and the influence of the solvent nature and the composition of the molecule/polymer on the separation performance are discussed. In the end, novel directions for fine-tuning the separation performance of ceramic membranes for solvent nanofiltration applications will be given.

Micro/Mesoporous ceramic membrane



$\varnothing_{\text{pores}} \sim 0.9\text{-}5\text{ nm}$

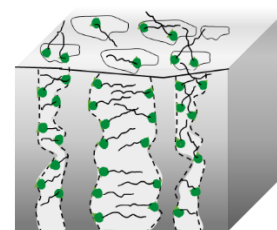
■ $\gamma\text{-Al}_2\text{O}_3$ matrix

▲ Unoccupied ceramic surface sites

Tuning the chemistry of the membrane pore surface!



Grafted ceramic membrane



$\varnothing_{\text{pores}} \leq 1.5\text{ nm}$

● Grafted polymer brush or molecule

Fig. 1 – Schematic illustration of the concept of grafted ceramic membranes.

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- (2) Dubreuil, M. F. S.; Servaes, K.; Ormerod, D.; van Houtven, D.; Porto-Carrero, W.; Vandezande, P.; Vanermen, G.; Buekenhoudt, A. Selective Membrane Separation Technology for Biomass Valorization towards Bio-Aromatics. *Sep Purif Technol* 2017, 178, 56–65. <https://doi.org/10.1016/j.vwseppur.2016.12.033>.
- (3) Merlet, R. B.; Pizzoccaro-Zilamy, M.-A.; Nijmeijer, A.; Winnubst, L. Hybrid Ceramic Membranes for Organic Solvent Nanofiltration: State-of-the-Art and Challenges. *J Memb Sci* 2020, 599. <https://doi.org/10.1016/j.memsci.2020.117839>.
- (4) Kyriakou, N.; Pizzoccaro-Zilamy, M. A.; Nijmeijer, A.; Luiten-Olieman, M.; Winnubst, L. Hydrolytic Stability of PEG-Grafted γ -Alumina Membranes: Alkoxysilane vs Phosphonic Acid Linking Groups. *Microporous and Mesoporous Materials* 2020, 307 (January). <https://doi.org/10.101>