Self-assembly of graphene oxide and polyelectrolyte complex nanohybrid membranes for nanofiltration and pervaporation

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Highlights

- Graphene oxide and polyelectrolyte complex (GO/PEC) nanohybrid membranes.
- Improvement of mechanical and thermal property with low loading of graphene oxide.
- GO membranes improved pervaporation selectivity by 6.88%.

Abstract

Organic–inorganic nanohybrids are believed to be one of the most promising new membrane materials for separation applications. In this study, a new nanohybrid membrane was prepared by incorporating graphene oxide (GO) into polyelectrolyte complexes (PECs). Poly(ethyleneimine)-modified GO and polyacrylic acid were sequentially assembled onto a hydrolyzed polyacrylonitrile ultrafiltration supporting membrane. The nanohybrid membranes were subsequently immersed in polyvinyl alcohol solutions and cross-linked by glutaraldehyde. The assembly process was systematically investigated by scanning electron microscopy, Fourier transform infrared analysis, an electrokinetic analyzer, a nano-indentation and thermogravimetric analyzer. The nanoindentation and thermogravimetric experiments in particular indicated that the GO incorporation greatly improved the Young’s modulus, hardness and thermal stability of the membranes. It was found that the resulting membranes had excellent dye removal capacity. The retention of Congo red could reach 99.5% with the permeance of 8.4 kg/m²h MPa. In the case of the separation of monovalent and divalent ions, such membranes show good nanofiltration properties. The retention of Mg²⁺ and Na⁺ were 92.6% and 43.2%, respectively. Additionally, it was demonstrated that this GO/PECs nanohybrid membrane is also a good candidate for the pervaporation dehydration of different solvent–water mixtures. The water content could be enriched from 5.0 wt.% (in the feed) to 95.4 wt.% (in the permeate) with the permeate flux of 268 g/m²h in the pervaporation of ethanol/water mixture (50/50).

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1. Introduction

Dense composite membranes have been widely used in many fields such as fuel ethanol manufacturing [1], recovery of organic solvents [2], water purification [3], dye removal [4], desalination [5], and gas and hydrocarbon separation [6–8]. The development of new membrane materials is still one of the central tasks in this field. Generally, polymeric membranes incorporate high-selective sorption and diffusion materials. However, many hydrophilic polymers swell or plasticize dramatically when exposed to hydrocarbons even in low concentrations. Moreover, the mechanical and thermal stability are needed to be improved [9]. In contrast, inorganic zeolite materials offer advantages such as high flux and no swelling and thus achieve a more constant performance with varying feed concentration. However, one major disadvantage of zeolite membranes is their brittleness, making them require a careful handling. Moreover, the non-zeolite pores crystal intergrowth or pin holes usually lead to low selectivity [10]. Therefore, organic–inorganic nanohybrids are believed to be one of the most promising future separation membrane materials.

In recent years, graphene oxide (GO), which is considered to have a one-atom thick, two-dimensional, closely packed honeycomb lattice [11–14], has attracted extensive attention for its remarkable electrical, physical, and mechanical properties. Much research is ongoing to investigate the applications of GO for nanoelectronic devices, transparent conductors, and composite materials [13]. For instance, Hong et al. demonstrated the nanoassembly