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Carbon-based building blocks for alcohol dehydration membranes with disorder-enhanced water permeability

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ABSTRACT

Graphene oxide (GO) thin films have demonstrated outstanding water permeability and excellent selectivity towards organic molecules and inorganic salts, unlocking a new exciting direction in the development of nanofiltration, desalination and pervaporation membranes. However, there are still high concerns about their stability at basic pH and under cross-flow conditions. The stabilization of graphene oxide can be achieved by thermal or chemical reduction; but stacked layers of reduced GO tend to form ordered and compact graphite-like structures, thus preventing their application as molecular separation membranes. In this work, a humic acid-like biopolymer (HAL), extracted from organic compost with a yield of ~20%, was used to fabricate composite GO-HAL membranes. The HAL brings a high degree of disorder to the membrane structure, with the benefit of an increased water permeation rate. Upon thermal stabilization, the membrane with a biopolymer loading of 30% presented an ideal water/ethanol selectivity of 45 and a water permeance that is 33% higher than the pristine graphene oxide membrane. The enhanced water permeability along with the good water/ethanol selectivity makes the GO-HAL membranes promising devices for alcohol dehydration technologies.

1. Introduction

The natural carbon cycle provides inexpensive sources for highly versatile building blocks in the development of new nanostructured materials for energy technologies and environmental applications [1–3]. In this work, the chemical similarity and the structural differences of graphene oxide (GO), derived from natural graphite, and that of a humic acid-like polymer (HAL), extracted with high yield from composted organic urban waste, are exploited to fabricate stable and homogenous carbon-based membranes (GO-HAL) with disorder-enhanced water permeability.

Unimpeded water permeation and high selectivity towards organic molecules have recently been reported for GO-based thin films [4–6], thus unlocking a new and exciting direction in the development of artificial membranes for water purification and alcohol dehydration technologies. The performances of GO membranes are even more astonishing, if we consider that water permeation occurs through a labyrinthic path in between overlaid individual GO sheets [7–11]. Indeed, this type of structure contrasts with the conventional design of membrane materials, which aims for low-tortuosity pores or channels through the membrane layer [12–14]. It has been speculated that the free water-permeation through GO membranes is due to the low-friction flow of water monolayers in between pristine graphene domains [4]. However, recent simulation studies [9–11] show that this "frictionless" transport is hampered by the side-pinning effect of the functional groups and of water molecules in the oxidized regions of the GO. Therefore, the water permeation mechanisms in GO membranes have not yet been clarified. Moreover, there are still high concerns about the mechanical stability of layered GO membranes under cross-flow conditions [15] and about their chemical pH stability due to the GO dynamic structure which leads to deoxygenation in an alkaline environment [16–19]. Reduction of the oxygen functional density (and thus stabilization of the GO structure) can be achieved by thermal or chemical methods. However, stacked layers of reduced GO (rGO) tend to form ordered and compact graphite-like structures with no permeability, thus preventing their application as molecular separation membranes. Hence, interlayer

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spacing and structural order appear to be the crucial parameters for molecular transport in GO and rGO membranes.

In this work, HAL was used to induce disorder in the graphene oxide membranes, and thus to increase their water permeability upon thermal stabilization, as shown in Fig. 1. HAL is formed by aerobic stabilization of organic urban waste [20,21]. HAL can be extracted from commercial compost with yields >20% and despite fluctuations in the composition of the starting waste, its chemical structure after long aerobic treatment (composting) times [22] is similar. Due to its amphiphilic properties, HAL has been proposed for several industrial applications including as a component for detergent formulations [23], as a textile auxiliary [24], as a photosensitizer for water decontamination [25,26] and in the preparation of composite plastics [27].

From a chemical point of view, both GO and HAL consist of a carbon backbone functionalized with oxygen-containing moieties (Fig. 1a and b) [28]. However, GO dispersions consist of 2D layers with monoatomic thickness, while dispersed HAL macromolecules have a 3D branched structure. In the current study, GO-HAL membranes with HAL contents ranging from 0 to 30 w% were fabricated by the drop-casting method. GO and HAL were obtained from natural graphite by a modified Hummers' method [29] and from a commercial compost by the Montoneri's method [20], respectively (Fig. 1c and d). Ammonia was added to facilitate the dissolution of the HAL, which has scarce solubility at acidic and neutral pH. Moreover, ammonia can facilitate cross-linking [30,31] during annealing. The dispersions were cast on glass Petri-dishes and the solvent was left to evaporate at room temperature for three days to form highly smooth, homogenous, and highly flexible membranes (Fig. 1e).

2. Experimental section

2.1. Synthesis of graphene oxide dispersions

All the chemicals used for the GO-HAL synthesis were purchased from Sigma–Aldrich, unless otherwise specified. 5.0 g of natural graphite powder (Stellenbosch University, Stellenbosch, SA) and 2.5 g of sodium nitrate (99%) were added to 115 mL of 98% sulfuric acid under vigorous stirring at 0 °C. While maintaining vigorous agitation, 15 g of potassium permanganate was added to the suspension. The rate of addition was carefully controlled to prevent the temperature of the suspension from exceeding 20 °C. The ice bath was removed and the temperature of the mixture was brought to 32 °C, where it was maintained for 30 min to obtain a paste. Then, 230 mL of MilliQ water was slowly added to the paste under stirring, causing a violent reaction and an increase in temperature. After maintaining the temperature at 98 °C for 15 min, the suspension was further diluted with 210 mL of aqueous hydrogen peroxide (3% V/V). The so-obtained product was recovered by

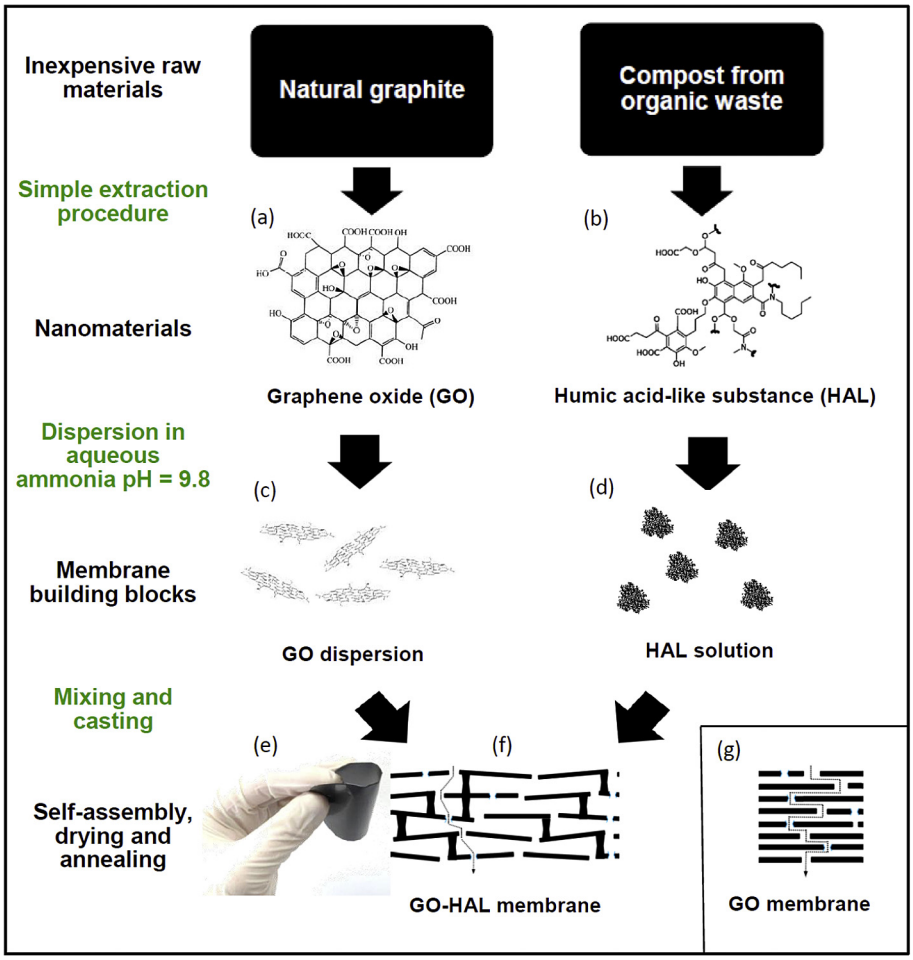

Fig. 1. Schematic representation of the fabrication of GO-HAL membranes: GO (a) and HAL (b) are extracted from natural graphite and organic compost, respectively. GO layers (c) and HAL polymer (d) are dispersed in aqueous ammonia. The two dispersions are mixed and cast on a Petri-dish to obtain GO-HAL membranes (e). After thermal annealing, the water transport path across these GO-HAL membranes (f) is less tortuous than is the case for a pure GO membrane (g). (A colour version of this figure can be viewed online.)