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Comparison of self-standing and supported graphene oxide membranes prepared by simple filtration: Gas and vapor separation, pore structure and stability

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ABSTRACT

A large series of self-standing and supported graphene oxide (GO) membranes were prepared via a facile synthetic approach involving the filtration of GO suspensions through polymeric and ceramic macroporous filters. Our overall aim was to develop a membrane that would be almost impermeable to helium and hydrogen, exhibiting in parallel very high water vapor and moderate alcohol vapor permeability, properties that constitute this type of membranes very promising for pervaporation and gas separation applications. Several of the derived self-standing membranes, especially those developed using aqueous GO suspensions of low concentration in GO, have met the above mentioned requirements. In particular, the development of highly efficient GO membranes using suspensions of low concentration ($\leq$ 1.0 g/L in order to achieve individual GO flakes rather than GO stacks) and of high volume ($>$ 50 mL to avoid very thin membranes which in turn incorporate defects) is straightforward and independent of the filtration rate, while slow filtration rates lead to better results when employing higher GO concentrations (1.5 g/L), but never to a membrane with purely molecular sieving characteristics. Small-angle X-ray scattering (SAXS) measurements indicated better GO's sheet packing and, thus, smaller pore size/network available for gas diffusion in membranes with smoother surfaces. In addition, the in-plane distance between adjacent GO sheets (especially on the outermost layer of the membrane), and also the size of GO stacks, were found to have more impact on the performance of the membranes than the respective d-distance determined by X-ray diffraction (XRD). Overall, a self-standing membrane developed by using anodised alumina (AAO) filter exhibited exceptional stability coupled with an excellent water vapor flux and water/alcohol selectivity.

1. Introduction

Flakes of graphene oxide (GO) can be arranged and stabilized in the form of structured layers, forming a GO membrane that incorporates nanoporous inter-flake galleries, having sufficient size to separate small gas molecules [1–4].

GO membranes, are usually produced by vacuum filtration [5], direct evaporation [6], spin-casting [7] and spray or spin coating [8,9] of aqueous GO suspensions on macroporous polymeric and ceramic filters. The co-existence of a large population of oxygen containing groups on the surface and especially at the edges of the single GO flakes [10] render the respective structured layers to be flexible, meaning that mass transport channels can be formed depending on the gas brought into contact with the membrane. This is the most plausible explanation for the permeation of water and alcohol vapors through GO membranes that are impermeable to much smaller molecules such as helium and hydrogen [11]. The increased electrostatic interaction between water and alcohols with the oxidized part of the flake causes the structured layer to open at the edges so that the vapor molecules achieve their intercalation between the GO flakes [12].

From this point and until their exit from the membrane, the intercalated molecules undergo unimpeded permeation that

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(especially in the case of water) has already been demonstrated experimentally [5,11] and explained theoretically by many different mechanisms. For instance, in close relation to what was concluded for water permeation into the bore channels of well aligned carbon nanotube membranes [13,14], the hydrophobic nature of the graphene sheets repels the water molecules from colliding with the pore walls, forcing them in a "single-file" diffusion mechanism through the core of the interlayer galleries [15].

Another plausible explanation derived from theoretical studies is based on the smoothness of the graphene surface. In the Knudsen type of diffusion, gas molecules permeate via collisions with the pore walls, and the post-collision velocity is distributed with probability proportional to $\cos\theta$ (θ, the angle of collision). In the case of a smooth surface such as that of graphene, the probability for a gas molecule that collides with the pore wall to be reflected to the direction of flow increases and this enhances significantly the flux [15].

The flow enhancement has also been attributed to the influence of nanoconfinement on the water conformation inside the pore channels. The water molecules form clusters that are weakly bound and undergo a concerted diffusion mechanism [16]. Recently, theoretical studies pointed-out that when water molecules interact with the oxygen containing groups of GO layers, the membranes are wedged open, resulting also to the opening of the pristine fraction of the GO layers [12]. The water molecules that enter this pristine graphene fraction of a layer, due to a negligible change in the free energy [12], are promptly squeezed out to bulk or oxidized parts, thereby creating channels of fast permeation.

Other theoretical studies, show skepticism as to the definite reason behind the enhanced water flux. These studies conclude possible breakdown of the fast water transport in GO due to the existence of oxygen functional groups that interact through hydrogen bonding with the water molecules [17]. As a result, the water transport through pristine graphene channels, established by nano-confinement, is retarded by a prominent side-interaction effect from flow paths hosting oxidized regions [18].

The aforementioned theoretical studies are very important as they can form the basis for future design of high-performance membranes for specific separation applications, as for example for gases and vapors with divergent influence of the interaction effect with the oxidized parts, such as polar and non-polar gases.

In parallel, systematic experimental work is required and is of paramount importance for achieving control on the pore structure and surface chemistry towards the development of tailor-made membranes exhibiting specific gas permeation and selectivity characteristics. Although there is a large number of experimental reports on self-standing GO membranes exhibiting outstanding gas separation [11] and water permeation performances [19], there is still a lack of systematic study aiming to conclude how the preparation conditions influence the gas and vapor permeation properties of the GO membranes. Therefore, more information on the overall approach and methodology towards optimization is urgently required.

In a previous study we have examined the effect of the filtration rate and GO's surface chemistry (amount of the oxygen-containing functional groups present along GO graphitic framework) on the gas permeability and pore structural characteristics of a series of 7 self-standing GO membranes developed with the vacuum filtration method [5]. The most important findings were that both parameters affect substantially the pore structure and, consequently, the separation capacity of the prepared membranes. In the present work, we have further broaden the spectrum of parameters under investigation for a series of more than 25 membranes, covering also: (i) the effects of varying the concentration of starting GO suspensions, (ii) using different types of substrates (rather than self-standing only); (iii) thoroughly studying the related properties of the derived membranes by methanol and isopropanol vapor permeability experiments (besides vapor water); and (iv) analysing not only the pore structure of the membranes but also their stability in contact with gas and vapor. The presentation of the results evolves by discussing on important findings regarding the influence of the substrate and of the in-plane distance between adjacent GO flakes located on the outermost layer of the membranes, providing in parallel generalised conclusions in regard to the preparation conditions that could assist the development of GO membranes with enhanced water flux and negligible gas permeability.

2. Experimental

2.1. Membrane preparation

The GO suspensions used in this work were synthesized from synthetic graphite (particle size $\leq 20\ \mu\text{m}$) through the Hummers, Brodie and Staudenmaier's methods.

The modified Hummers method [20–22] involved the addition of 5 g of graphite and 5 g of sodium nitrate onto 240 mL of sulphuric acid, under constant agitation and in an ice-bath. Then, 30 g of potassium permanganate was added slowly to the mixture. The suspension was continuously stirred overnight at 35 °C. Afterwards, 1250 mL of water was added, followed by 35 mL of H_2O_2 (30% v/v). The suspension was filtered to remove the excess of acid and the oxidized material was then centrifuged (30 min at 3000 rpm) several times with distilled water until reaching a constant (near neutral) pH for water.

The procedure for the Brodie method [23,24] consisted on mixing 5 g of graphite and 100 mL of nitric fuming acid, under continuous agitation at 0 °C in an ice bath. Next, 40 g of potassium chlorate was added slowly to the mixture and stirred for 18 h at 0 °C. Subsequently, distilled water was added and the mixture was filtered under vacuum until a neutral pH of the filtrate was reached. The resulting Brodie and Hummers pastes were dried in a vacuum oven overnight at 80 °C. Then, the graphite oxide powder was dispersed in deionized water and sonicated with an ultrasonic processor (UP400S, 24 kHz) for 1 h. The undissolved solids were removed by centrifugation for 30 min at 3000 rpm. To stabilize the Brodie GO dispersion, the powder material was dispersed in a 0.01 mol/L sodium hydroxide solution as reported elsewhere [25]. The GO suspensions (1g/L) were used to produce membranes by vacuum filtration.

Reduced graphene oxide (rGO) was obtained by chemical reduction using the aqueous dispersion of GO (prepared by the modified Hummers method) and vitamin C as reducing agent [26,27]. Briefly, the GO suspension (0.1 g/L) containing the reducing agent (2 mmol/L) was heated at 95 °C for 3 h under vigorous stirring. The pH of the GO dispersion was adjusted to 10 with a 25% ammonia solution before the reduction process to promote the colloidal stability of the GO sheets through electrostatic repulsion.

GO was also synthesized using a modified Staudenmaier's well-established and widely accepted method [28–30]. In brief, a quantity of synthetic graphite was added to a mixture of concentrated sulphuric/nitric acid under cooling in an ice bath. Next, potassium chlorate powder was added to the mixture and the reaction was quenched after 18 h. The oxidation product was washed with distilled water until pH=7 and dried under vacuum at 40 °C overnight. The resulting powder was then dispersed in distilled water (5 g/L) and sonicated in an ultrasound bath (Branson 3510, 40 kHz) for 30 min to obtain the corresponding suspensions.

The GO membranes prepared are labelled as follows: *x*-GO-*i*-*y*-*z*-*v*, where: "*x*" indicates whether the membrane is supported