# Carbon-based building blocks for alcohol dehydration

*GO-HAL membranes*

Boffa, Vittorio; Mallon, Peter E.; Magnacca, Giuliana



*Publication date:*
2016

# Carbon-based building blocks for alcohol dehydration: GO-HAL membranes

Vittorio Boffa,[a,*] Peter E. Mallon,[b] Giuliana Magnacca.[c]

(a) Department of Chemistry and Bioscience, Aalborg University, Fredrik Bajers Vej 7H, 9220 Aalborg Øst, Denmark. e-mail: vb@bio.aau.dk
(b) Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa;
(c) Dipartimento di Chimica, NIS centre, Universitá di Torino, Via P. Giuria 7, 10125 Torino, Italy

MAT4TREAT New materials for water treatment

A biopolymer (HAL), extracted from organic compost with yield ~20%, was used to fabricate composite HAL-graphene oxide (GO) membranes. Upon thermal stabilization, HAL brings high disorder in the membrane structure, thus increasing water permeability. This feature together with the good water/ethanol perm-selectivity make GO-HAL membranes promising devices for alcohol dehydration.

## 1. GO-HAL fabrication

The natural carbon cycle provides inexpensive sources for highly versatile building blocks in the development of new nanostructured materials for energy technology and environmental applications. In this study, graphene oxide (GO) and a humic-like substance (HAL) were extracted from natural graphite[(1)] and organic compost,[(2)] respectively (Fig. 1). GO sheets and HAL macromolecules were dispersed in aqueous ammonia. The two dispersions were mixed to obtain GO-HAL mixtures with a HAL weight fraction from 0 to 30%. Thin membranes were formed by drop-casting. After thermal stabilization, the water transport path across this GO-HAL membrane is expected to be less tortuous than the one in a pure GO membrane, thus allowing for fast water permeation .

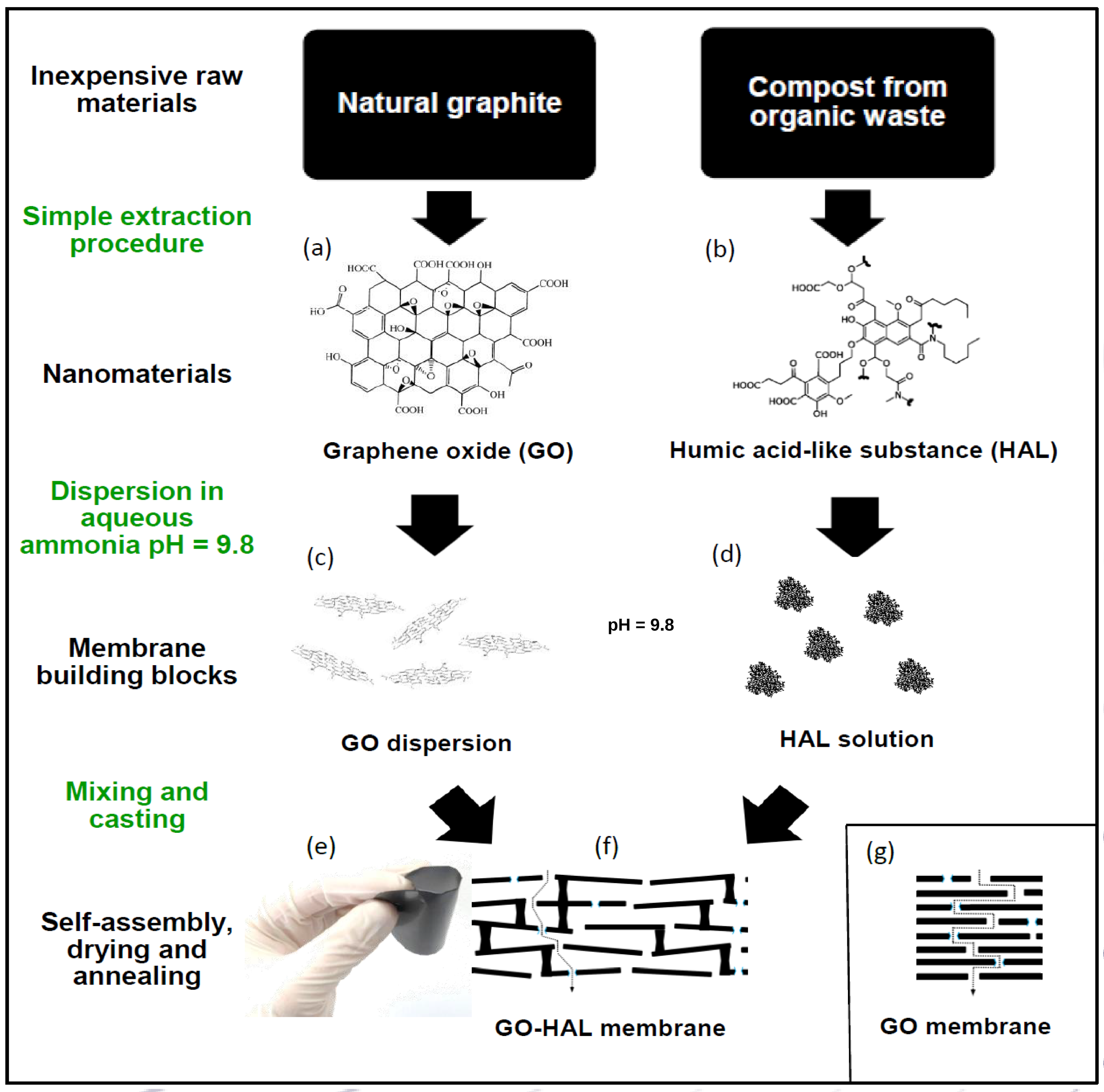


**Fig 1.** Schematic representation of the fabrication of GO-HAL membranes.

## 2. GO-HAL structure

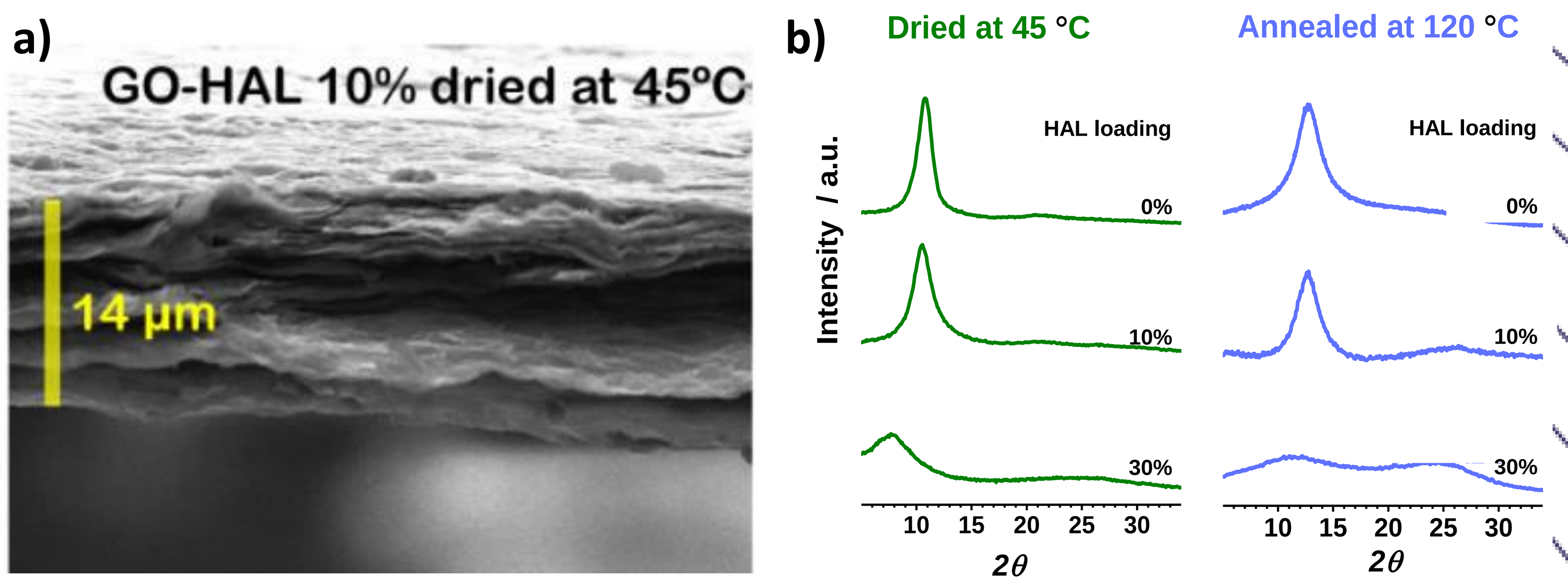


**Fig 2.** SEM (a) and XRD (b) analyses of selected GO-HAL membranes.

The typical lamellar structure of GO-HAL is depicted in Fig. 2a. From the chemical point of view, both GO and HAL consist of a carbon backbone functionalized with oxygen-containing moieties (i.e. carboxylic acids, phenols, and epoxy groups), which make them highly dispersible in water at neutral and basic pH. However, GO dispersions consist of 2D layers with monoatomic thickness, while dispersed HAL macromolecules have a 3D brunched structure. Due to their chemical resemblance, HAL macromolecules and GO sheets can easily intercalate during membrane formation, as shown by the XRD patterns of the GO-HAL with 30% HAL loading in Fig. 2b.

GO-HAL membranes resulted water-stable after annealing at 120 ºC and hydrophobic after thermal reduction at 200ºC .

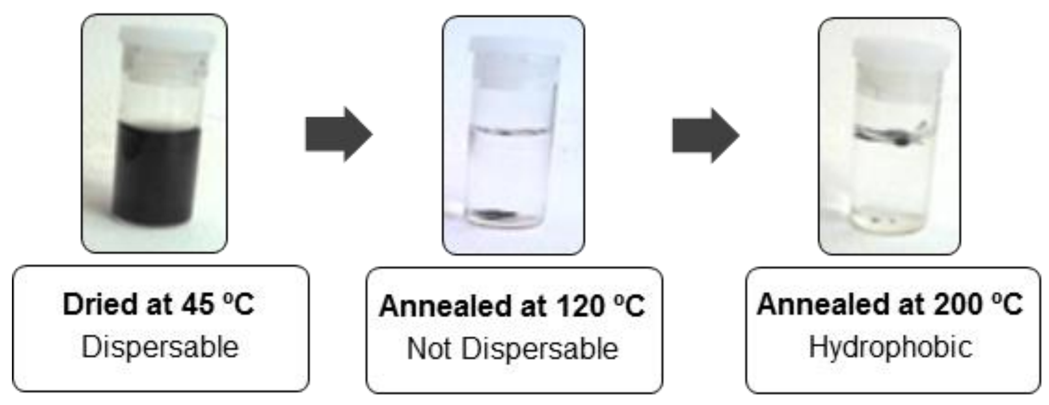


**Fig 3.** Dispersion test.

## 3. Alcohol dehydration GO-HAL

Permeation tests were performed with a simple method inspired by the previous experiment of Nair et al.[(3)] and Bounos et al.[(4)] The slop of the water mass loss of vials sealed with GO-HAL membranes did not change over the 48 h (Fig. 4a), indicating that the water vapour flow rate is constant and that the steam exposure did not caused structural changes in GO-HAL.

The permeance values of the membranes dried at 45 ºC and annealed at 120 ºC are plotted as a function of the HAL loading are plotted in Fig. 4b, two different trends are found. After stabilization at 120 ºC, high HAL loadings cause the membranes to have a more disordered and less dense structure, thus facilitating water permeation across the membrane. Also ethanol permeance increased with HAL loading (Fig. 4c). Despite that, the membrane with a HAL loading of 30% showed a water/ethanol permselectivity of 45 ± 10 and hence it is able to combine high water permeability and good alcohol retention.

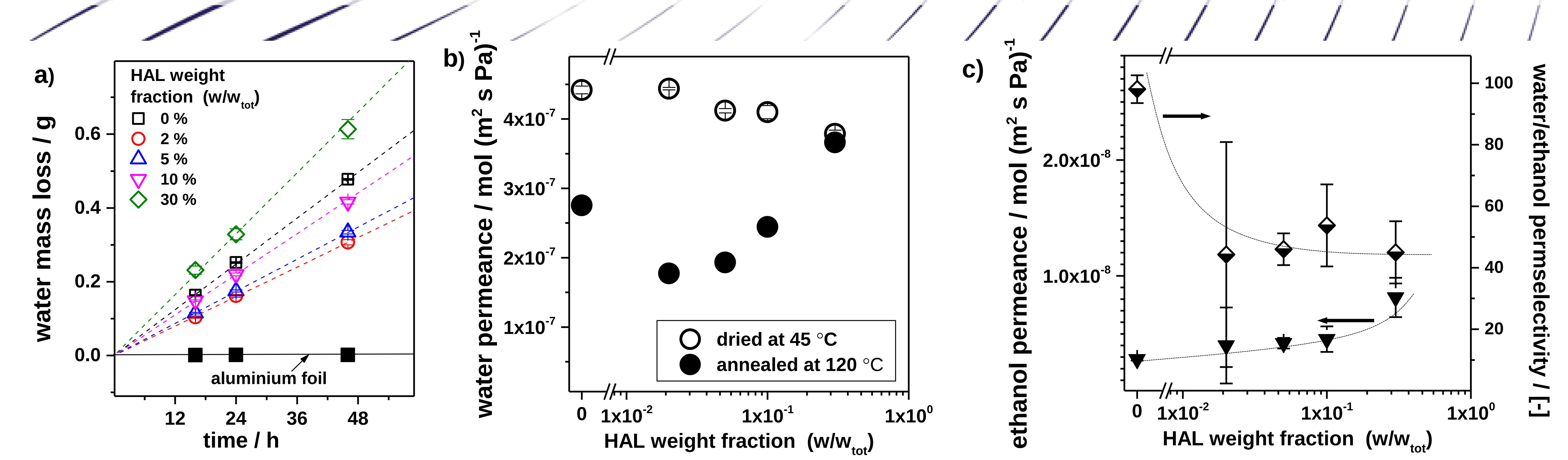


**Fig 4.** Permeation tests: (a) water mass loss at 40 ºC in vials sealed with GO-HAL membranes and with a dense aluminium foil as reference; (b) water permeance at 40 ºC for GO-HAL membranes dried at 45 ºC and stabilized at 120 ºC as a function of the HAL loading in the membrane material; (c) ethanol permeance and water/ethanol permselectivity at 40 ºC of GO-HAL membranes stabilized at 120 ºC as a function of the HAL loading in the membrane material.

## 4. Conclusions

In summary, the chemical similarity and the structural difference of graphene oxide (GO) and of a natural biopolymer (HAL) have been exploited to fabricate stable and homogenous carbon-based membranes with enhanced water permeability. This feature together with a good water/ethanol perm-selectivity makes GO-HAL membranes promising devices for alcohol dehydration.[(5)] This work was made possible by **project 645551, H2020-MSCA-RISE-2014.**

## References

[(1)]E. Montoneri, V. Boffa, P. Savarino, D.G. Perrone, G. Musso, R. Mendichi, M. R. Chierotti, R. Gobetto, ChemSusChem, 2009, 2, 239. [(2)]H.M. Etmimi, P.E. Mallon, Polymer, 2013, 54, 6078. [(3)]R.R. Nair, H.A. Wu, P. N. Jayaram, I. V. Grigorieva, A.K. Geim, Science, 2012, 335, 442. [(4)]K.S. Andrikopoulos, G. Bounos ,D. Tasis , L. Sygellou, V. Drakopoulos, G. A. Voyiatzis, Adv. Mater. Interfaces 2014, 1, 1400250. [(5)]V. Boffa, H. Etmimi, P.E. Mallon, H.Z. Tao, G. Magnacca, Y. Z. Yue, Disorder-enhanced permeability in graphene oxide membranes for alcohol dehydration, submitted.