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

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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 permselectivity 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.

2. GO-HAL structure

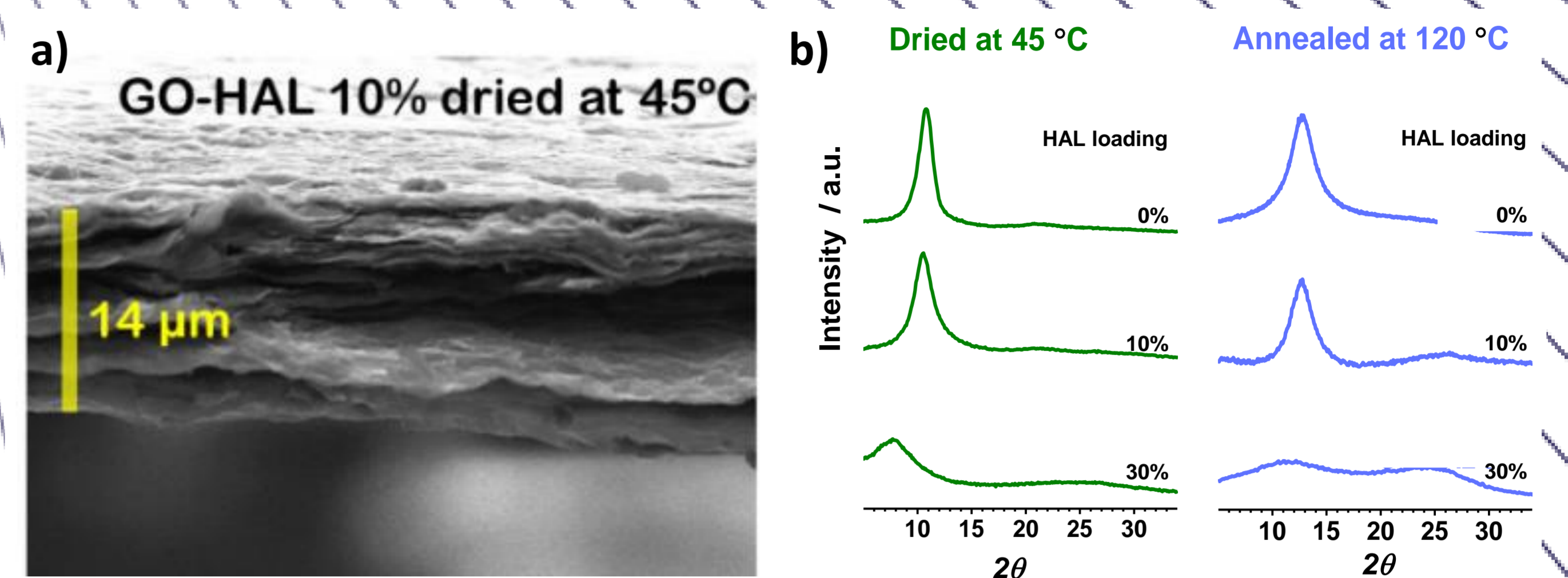


Fig 2. SEM (a) and XRD (b) analyses of selected GO-HAL membranes.

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 branched 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 °C and hydrophobic after thermal reduction at 200°C.

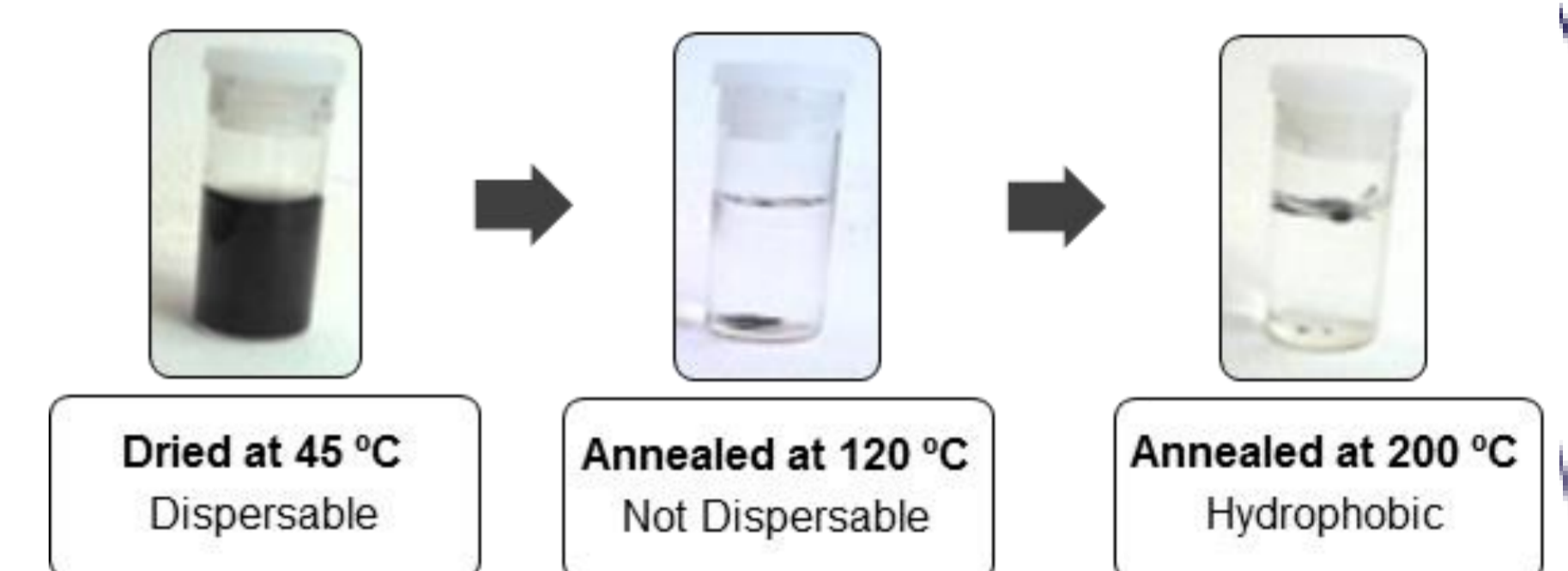


Fig 3. Dispersion test.

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 slope 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 cause structural changes in GO-HAL.

The permeance values of the membranes dried at 45 °C and annealed at 120 °C are plotted as a function of the HAL loading in Fig. 4b, two different trends are found. After stabilization at 120 °C, 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.

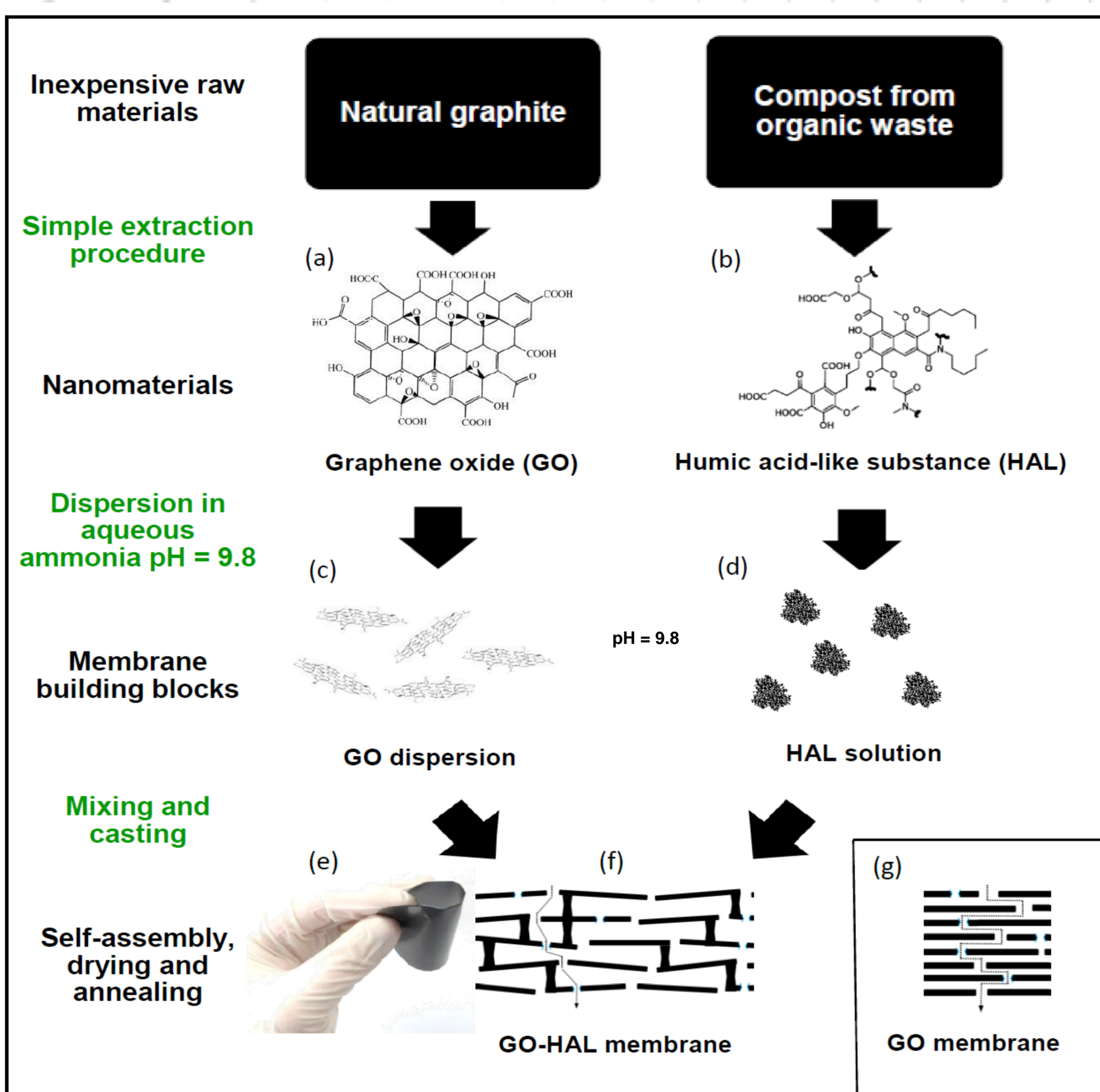


Fig 1. Schematic representation of the fabrication of GO-HAL membranes.

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.

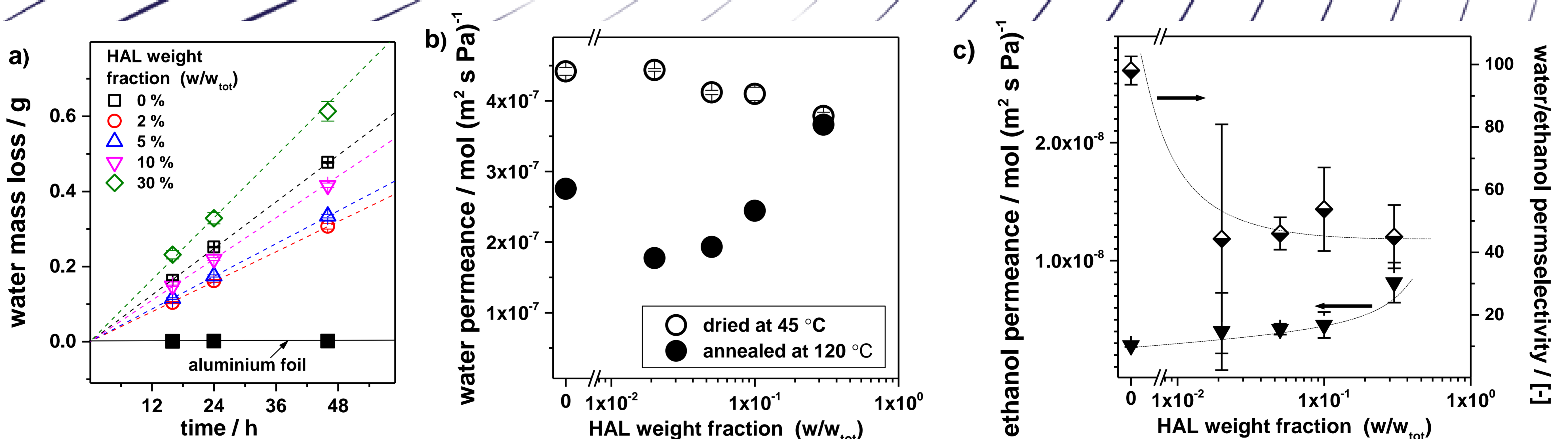


Fig 4. Permeation tests: (a) water mass loss at 40 °C in vials sealed with GO-HAL membranes and with a dense aluminium foil as reference; (b) water permeance at 40 °C for GO-HAL membranes dried at 45 °C and stabilized at 120 °C as a function of the HAL loading in the membrane material; (c) ethanol permeance and water/ethanol permselectivity at 40 °C of GO-HAL membranes stabilized at 120 °C 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 permselectivity makes GO-HAL membranes promising devices for alcohol dehydration.⁽⁵⁾ This work was made possible by **project 645551, H2020-MSCA-RISE-2014**.

References

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