**Tuning the molecular architecture of 2D GO-based nanocomposites  
for gas separation application**

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**1.Introduction**

Graphene Oxide (GO) is a 2D material derived from graphene oxidation and consists in a single sheet of graphite, functionalized by different oxygen-containing groups [1]. Thus, contrary to graphene, dispersion of GO can be easily accomplished in water, allowing a green and sustainable processability [2]. Among several possible applications, atomic-thick graphemic sheets spurs utilization in technological applications that demand 2D geometry, as fabrication of composite membranes for separation processes [3]. Ultrathin 2D composite membranes can be obtained by Layer-by-Layer (LbL) self-assembly [4], alternating the deposition of negatively charged GO and polycations [5], eventually leading to a layered molecular architecture with high order degree. In this work, we successively prepared nano-thick multilayers for gas-sieving applications such as hydrogen purification or pre-combustion carbon capture. The focus is on the gas couple He/CO2, using He as a safer H2 analogue, aiming to enhance the separation performances of existing membranes [6]. Furthermore, we demonstrated that membrane properties and performances can be conveniently modified by tuning the LbL procedure parameters or post-fabrication multilayers treatment that affect the 2D architecture, and consequently the gas sieving mechanism.

**2. Methods**

All chemical species were used as received. LbL self-assembled coatings were deposited on commercial polyimidic solvent-cast films (Matrimid® 5218) [7], used as substrate, and then superficially hydrolyzed, to allow self-interactions with charged species. LbL self-assembly was performed with a home-made apparatus following a previously reported procedure [4]. Briefly, Matrimid films were dipped in the polycation water solution (0.1wt%) for 5 minutes. Excess of deposited polycation was removed by a 20 min rising in neutralized water (pH = 7). Then, film was dipped in the GO water suspension (0.01wt.%) for 5 minutes and, once again, excess of deposited species removed with a 20 min rising in neutralized water. By repeating this procedure for 10 times, a coating of 10 BiLayers (BLs) was successfully prepared. Finally, coated films were hetaed for 30 minutes under an IR lamp to remove residual water in the coating.  
Gas transport properties of prepared coatings were evaluated with pure gas, by means of a manometric technique (ASTM D 1434). All the permeance were valued at 35°C. Permeances of the only coating (*GPCc*) were calculated from the experimentally determined value of permeance (*GPUTot*) excluding the effect of the Matrimid (*GPUM*) by means of the series resistance equation. All the presented results are the average of at least three analyses independently measured.

**3. Results and discussion**

LbL technique offers a large array of variables that can be opportunely tuned to modulate final molecular architecture, and thus modifying the resulting gas transport properties. The self-assembly with two different polycations (PEI or PDDA) lead to the fabrication of multilayers characterized by diverse perm-selectivities (Figure 1a). Indeed, while comparable values of selectivity were calculated for both multilayers, utilization of PDDA lead to a more permeable, and more attractive, coating. Interestingly, SEM imaging reveals that a smother surface was achieved when self-assembly was assisted by PDDA (Fig. 1b and c).



**Figure 1.** a) Perm-selectivity of the two differently self-assembled coatings; b) chemical structure of PEI and SEM image of outmost layer; c) chemical structure of PDDA and SEM image of outmost layer.

Even the possibility to accomplish post-fabrication modification was explored. Specifically, it is well known that an anoxic thermal annealing of GO results into its reduction (r-GO). Such conversion alters the structure of the multilayer, and the resulting transport phenomena. Water contact angle measurement confirm a gradual conversion of deposited GO into r-GO (increasing of the contact angle, Figure 2b). Interestingly, a 105°C (under vacuum) treatment lead to an improvement of perm-selectivity properties, while increasing the temperature a significant loss in selectivity was observed (Figure2a).



**Figure 2.** a) Perm-selectivity of differently post-fabricated annealed coatings; b) Water Contact Angles recorded for the outmost layers.

**4. Conclusions**

We presented a reproducible and scalable technology to self-assemble layered coating based consisting in an alternated deposition of a polycation and GO. Successively, we explore potential application of our multilayers as membrane for gas-sieving application, focusing our attention on the couple He/CO2, and good results were obtained. Moreover, by performing proper modifications, a modulation of the coating nature was accomplished and perm-selectivity properties could be improved.

**References**

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