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PIM-1/graphene pervaporation membranes for bioalcohol recovery

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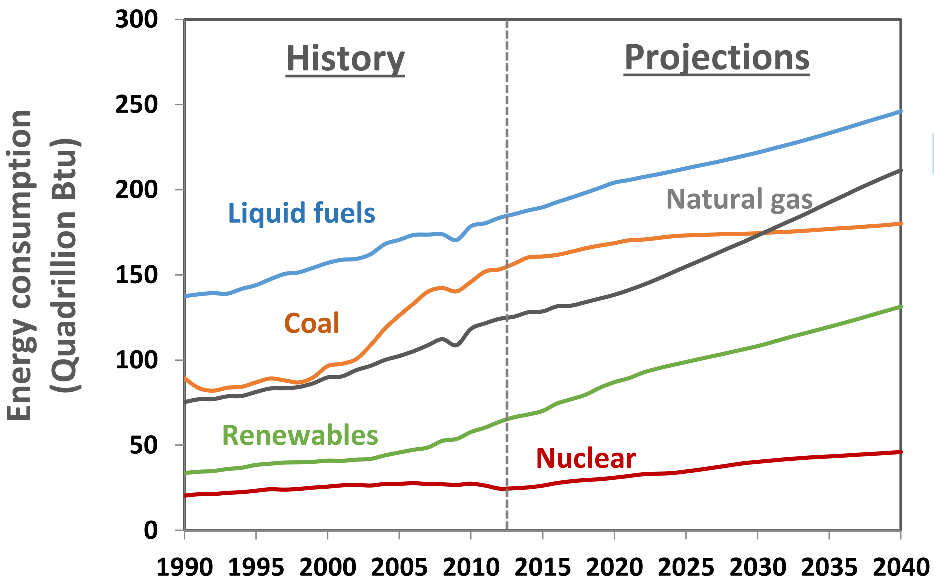
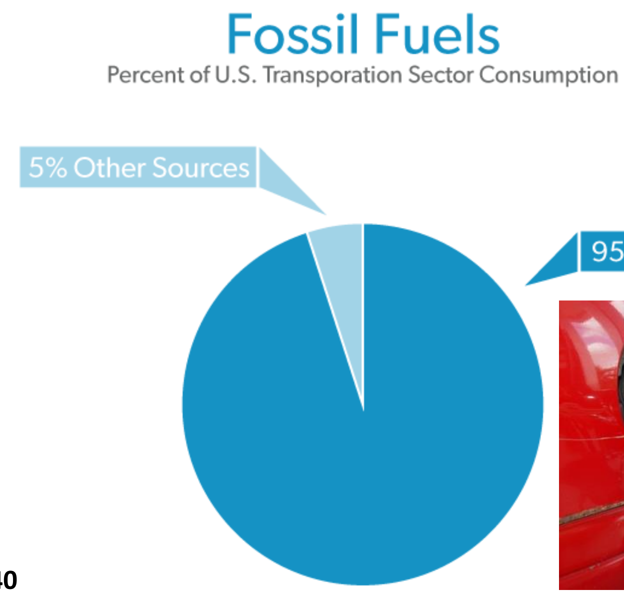
Motivation: energy sector and transportation



Source: EIA, International Energy Outlook, May 2016



Source: EIA, MER, March 2016

IER INSTITUTE FOR ENERGY RESEARCH

- The demand for energy requirement is increasingly growing.
- It is difficult to reach the world energy demand only by using fossil fuel

Alternative: BIOFUELS

Biofuels: definition and facts

The University of Manchester

A biofuel is any fuel source that is made from biological materials. The two most common kinds of biofuels are both gasoline alternatives: ethanol and biodiesel.

A Volkswagen Golf model that uses E10 blended bioethanol

The Ferrari F430 Spider Bio Fuel Concept car runs on E85 biofuel

The Saab BioPower runs on E85 which has higher octane rating than petrol

- ✓ Reduces greenhouse gas emissions as the release of CO_2 from burning the biofuels is matched by the CO_2 absorbed by the plants growing the biomass used to produce it
- ✓ Using so-called second-generation technologies to convert material such as crop residues into bioenergy can avoid competition for land

Biofuels: how can membrane technology help?

Bioethanol and biobutanol are produced via ferementation of biomass.

Biomass (cellulose, hemicellulose, lignin) → **Pre-treatment/ Enzymatic hydrolysis** → **Removal of Lignin** → **Sugar monomers** → **Fermentation** → **Solvent recovery** → **Bioalcohol < 0.5% water**

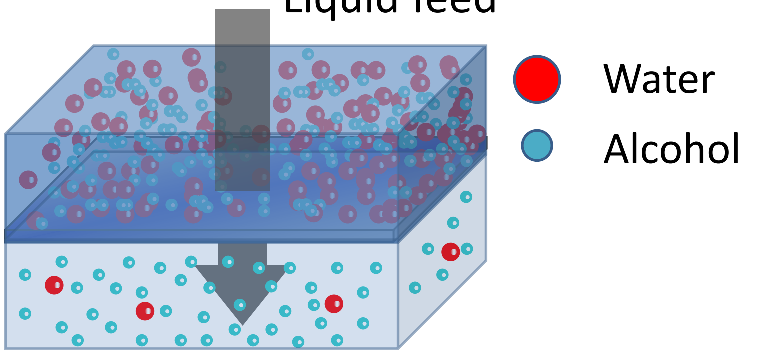
End-product inhibition is caused by the toxicity of the alcohol produced on the bacteria.
A concentration of less than 2% of bioalcohol (ABE fermentation process for biobutanol production) is typically achieved.

The bioalcohol needs to be purified from the fermentation broth (contains mainly water) by a series of distillation columns → 60-80% of the total production costs.

Step 1: Removal of alcohol form fermentation broth → **Step 2**: Further purification of alcohol

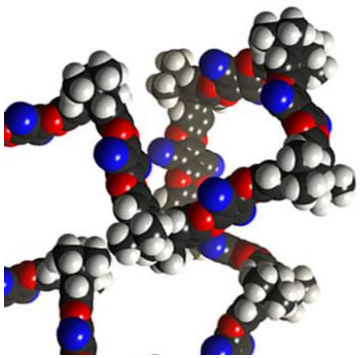
Organophilic membranes — Hydrophilic membranes

Organophilic pervaporation membranes



- **Inorganic membranes**, zeolites: silicalite-1, ZSM-5
- **Polymeric membranes**, polydimethylsiloxane (PDMS), poly[1-(trimethylsilyl)-1-propyne] (PTMSP), PEBA, PTFE
- **Hybrid membranes,** polymer matrices containing selective fillers e.g. silicalite-silicon rubber

Polymers of intrinsic microporosity (PIMs)



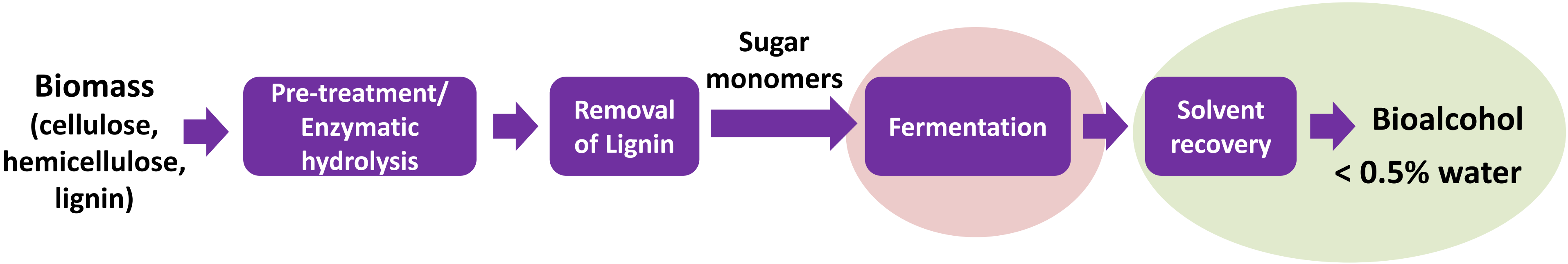
A continuous network of interconnected intermolecular voids, which forms as a direct consequence of the shape and rigidity of the component macromolecules.

N.B. McKeown & P.M. Budd, *Macromolecules*, 2010, **43**, 5163.

- ❑ Swelling in the presence of organic solvents → Reduction of the selectivity
- ❑ Ages over time → Increase in selectivity and reduction of flux

Biofuels: how can membrane technology help?

Bioethanol and biobutanol are produced via feremenation of biomass.



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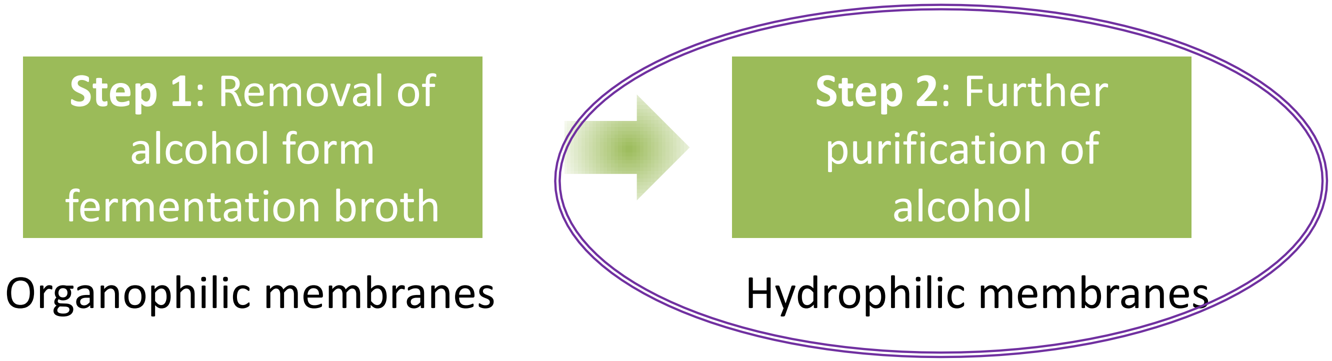
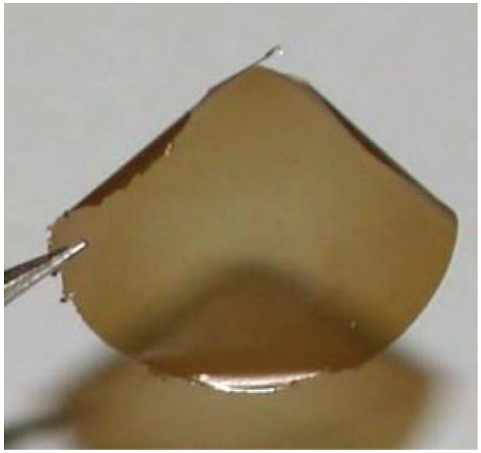
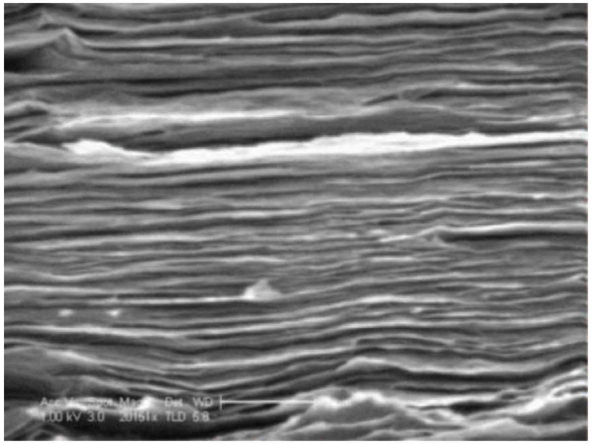
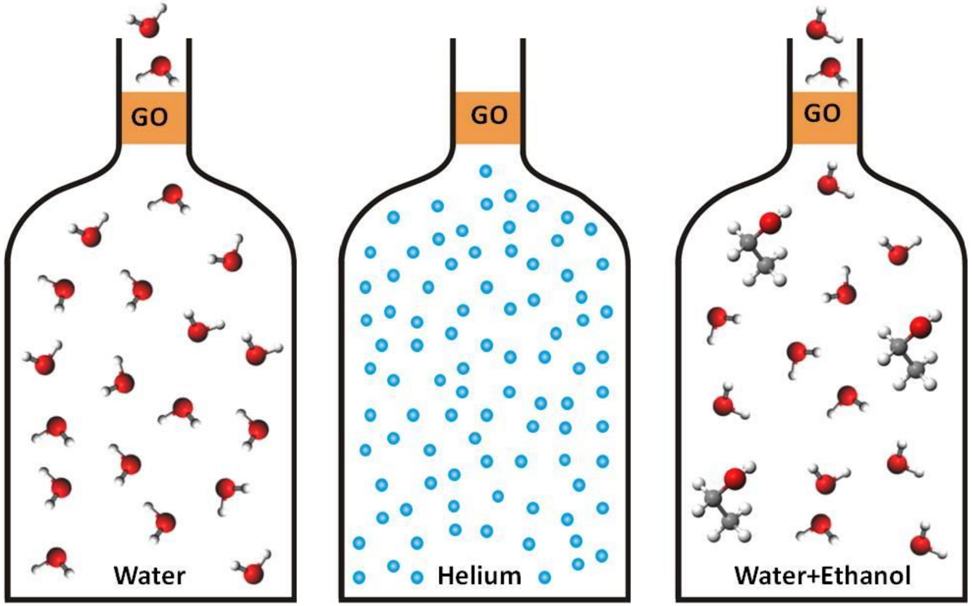
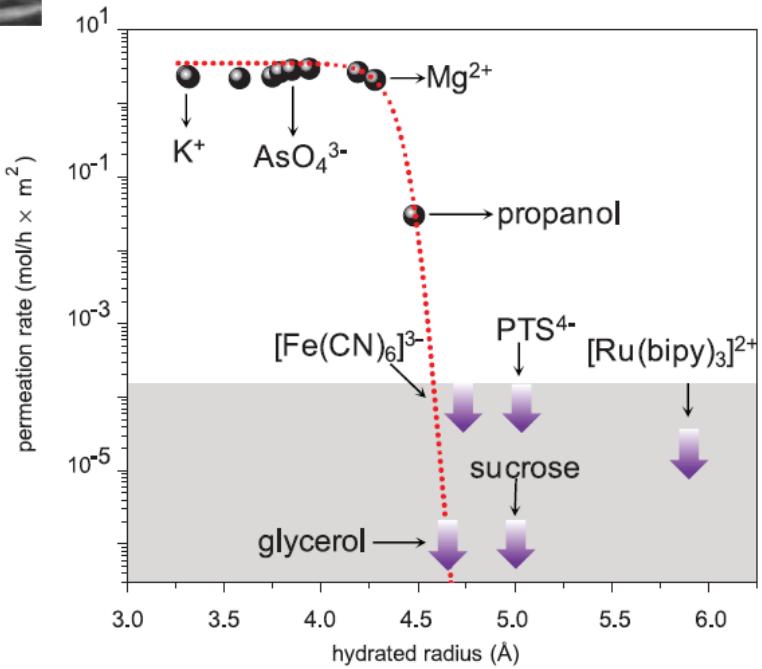


Hydrophilic graphene oxide (GO) membranes





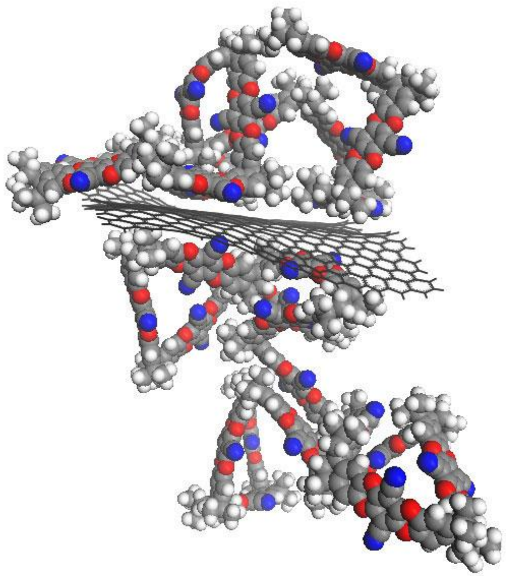




R. R. Nair et al. *Science*, ***2012,*** 335, 442 R.K. Joshi et al. *Science*, ***2014***, 343, 752

PIM-1 membranes with graphene

Simulations



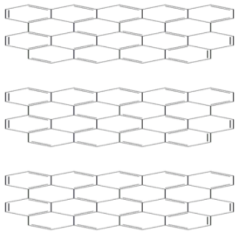
A. Gonciaruk et al., Micropor. Mesopor. Mater., 209 (2015) 126-134

Experimental work

- PIM-1 is soluble just in few organic solvents, ($CHCl_3$, THF, DMAc)
- Direct mechanical exfoliation of graphite in these solvents is not good
- GO and rGO flakes prepared via oxidation of graphite cannot be dispersed

Functionalization of GO with alkylamines can lead to monolayer and few-layered graphene flakes that are easily dispersed in $CHCl_3$

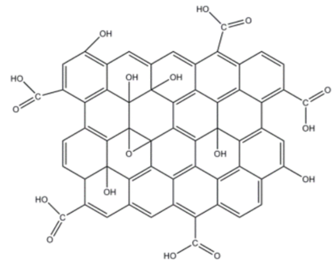
Preparation of graphene-like flakes



Graphite

Oxidation

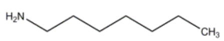
Hummers modified method



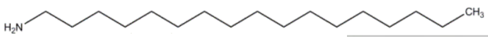
Graphene Oxide (GO)

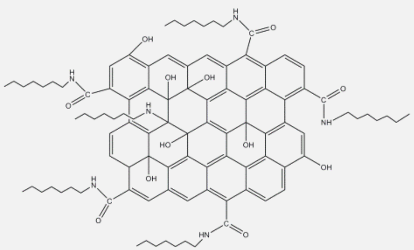
Functionalization

Octylamine (OA)

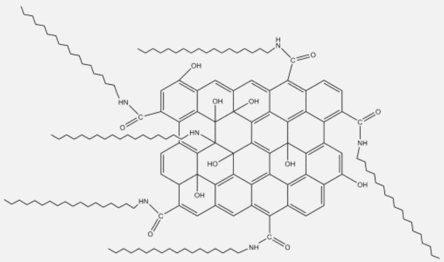


Octadecylamine (ODA)



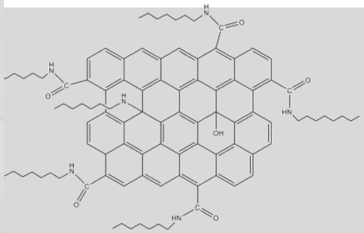


GO-OA



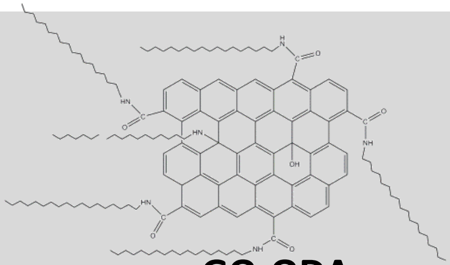
GO-ODA

Chemical reduction (hydrazine)



rGO-OA

D. Li, et al., *Nature Nanotechnology*, ***2008**, 3*(2), 101-105



GO-ODA

Characterization of graphene-like flakes: FTIR

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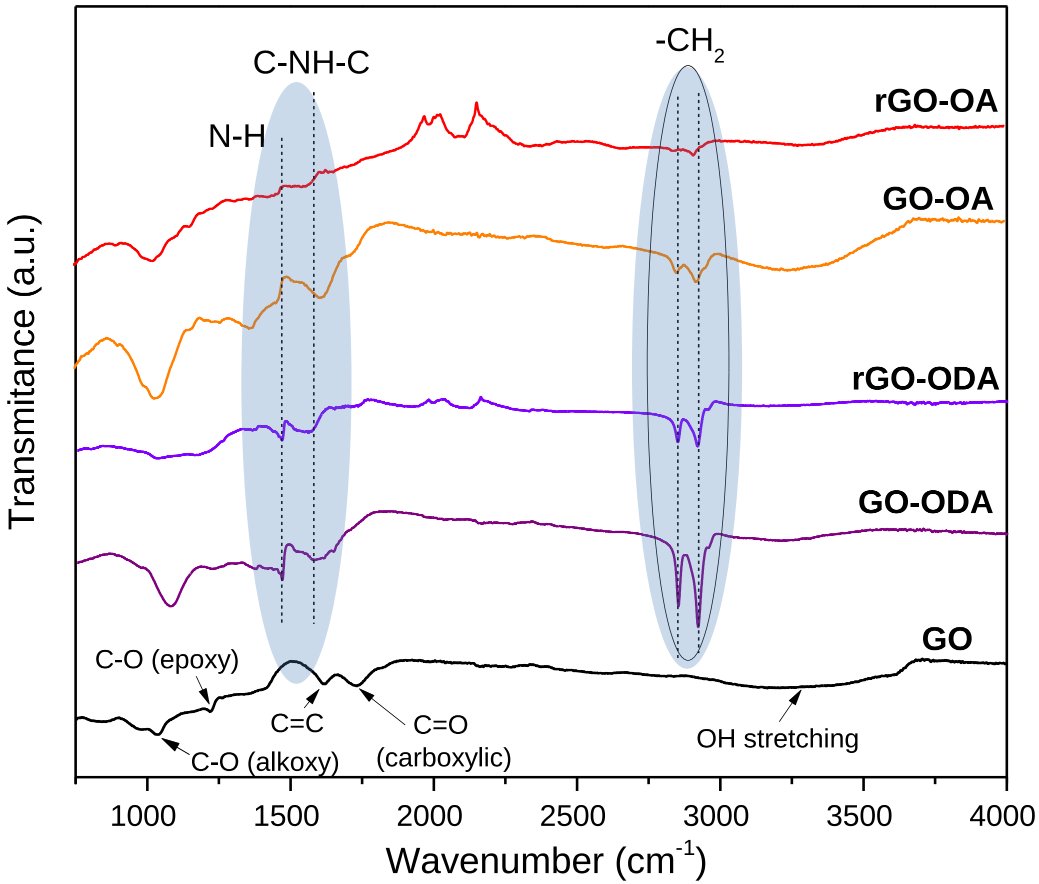
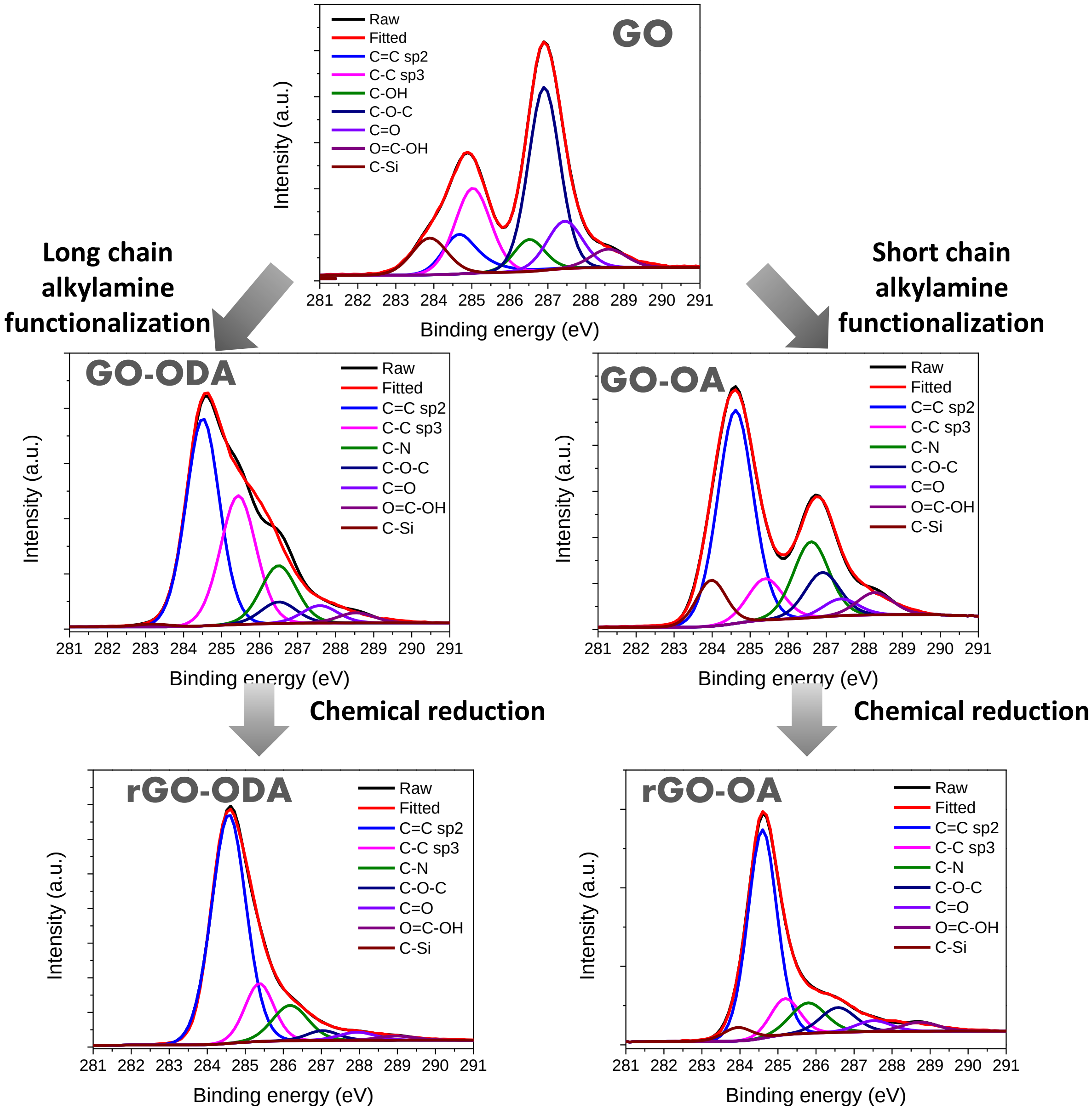


Peaks at 2850/2920 cm^{-1} → -CH_2 of alkylamines

Decrese in intensity for reduced samples → loss of some alkylamine upon treatment with hydrazine

Peaks at 1470 cm^{-1} and 1580 cm^{-1} → covalent bonds (C-N-C) between alkylamines and GO

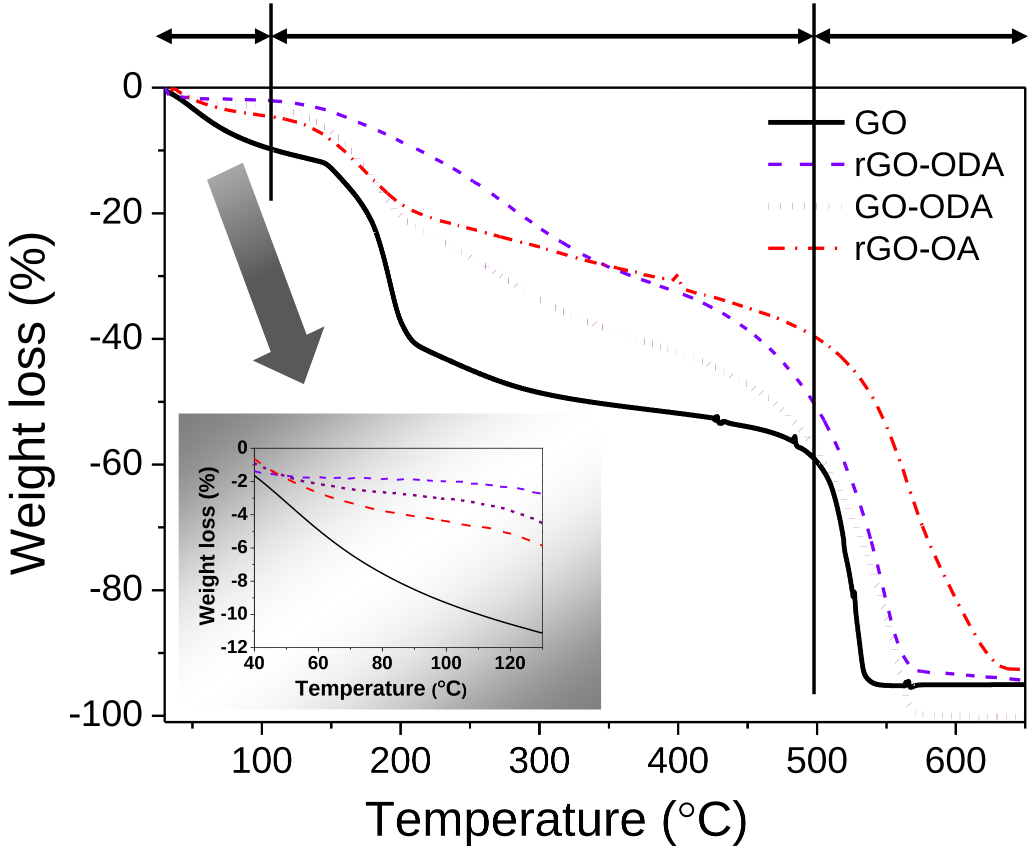
Characterization of graphene-like flakes: XPS



Filler	C:O ratio
GO	1.74
GO-ODA	13.8
rGO-ODA	12.9
GO-OA	4.80
rGO-OA	3.80

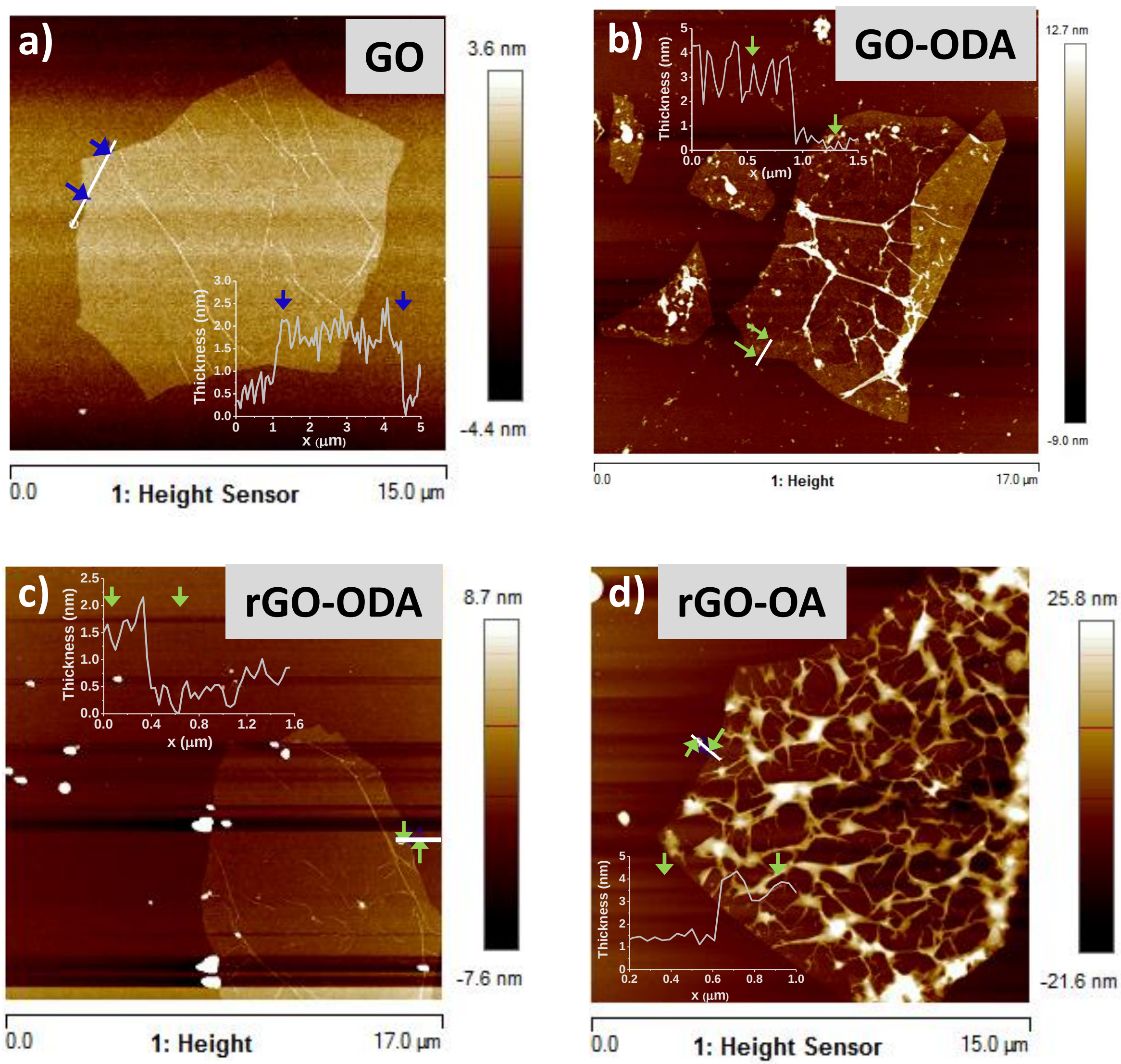
- ✓ The higher C:O ratio corresponds to the sample functionalised with the alkylamine that has the longer chain
- ✓ C:O ratio decreases upon chemical reduction as a result of a small portion of the grafted alkyl chains being removed.

Characterization of graphene-like flakes: TGA



- Enhancement in the hydrophobicity degree of starting material GO in this order: rGO-ODA > GO-ODA > rGO-OA
- Presence of both physically adsorbed and chemically bonded ODA to the GO flakes
- Weight loss for rGO-ODA > rGO-OA as ODA chains having larger mass

Characterization of graphene-like flakes: AFM

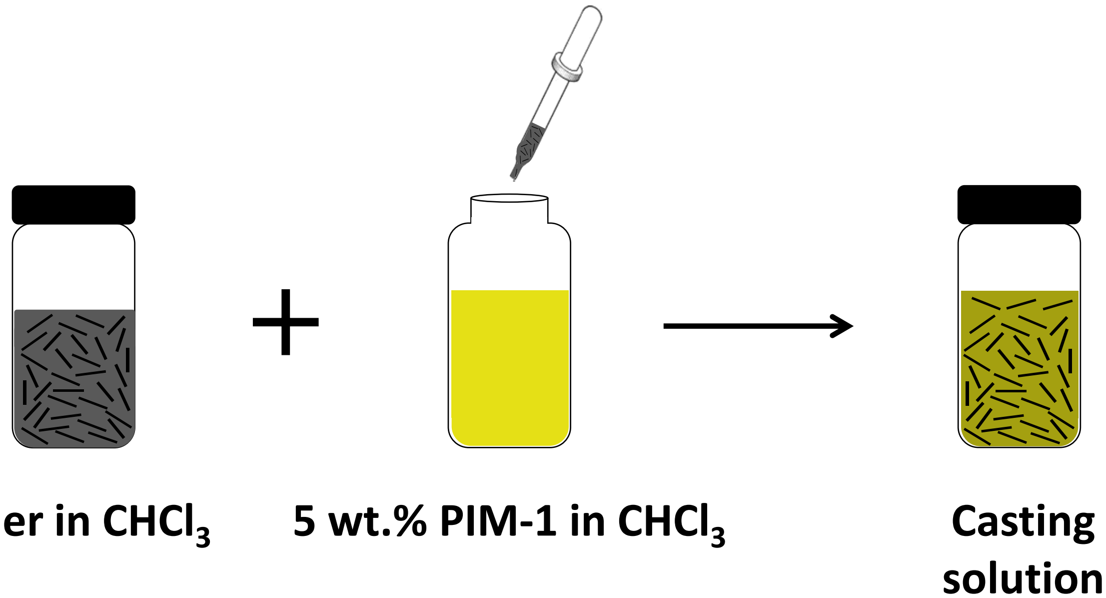


lateral dimensions of GO sheets are in the expected range with flakes of sizes ranging from few tens of nanometers to few micrometers

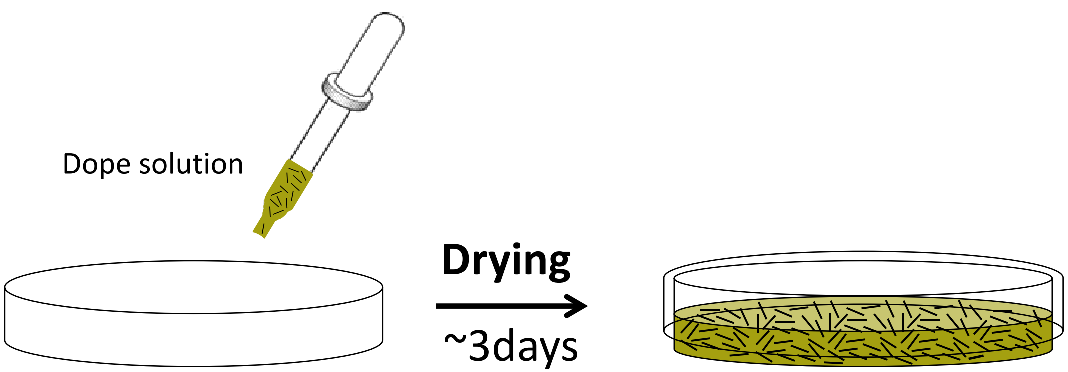
monolayer and few-layered structures are observed

1. Preparation of casting solutions

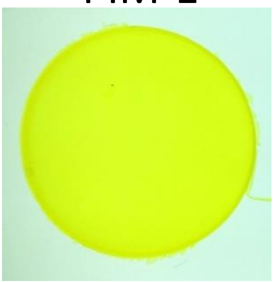
wt.%	Filler
0.01	rGO-ODA
0.05	GO-ODA
0.1	rGO-OA
1	



2. Casting-evaporation on flat petri dishes



PIM-1



PIM-1 + rGO-ODA

Membrane fabrication

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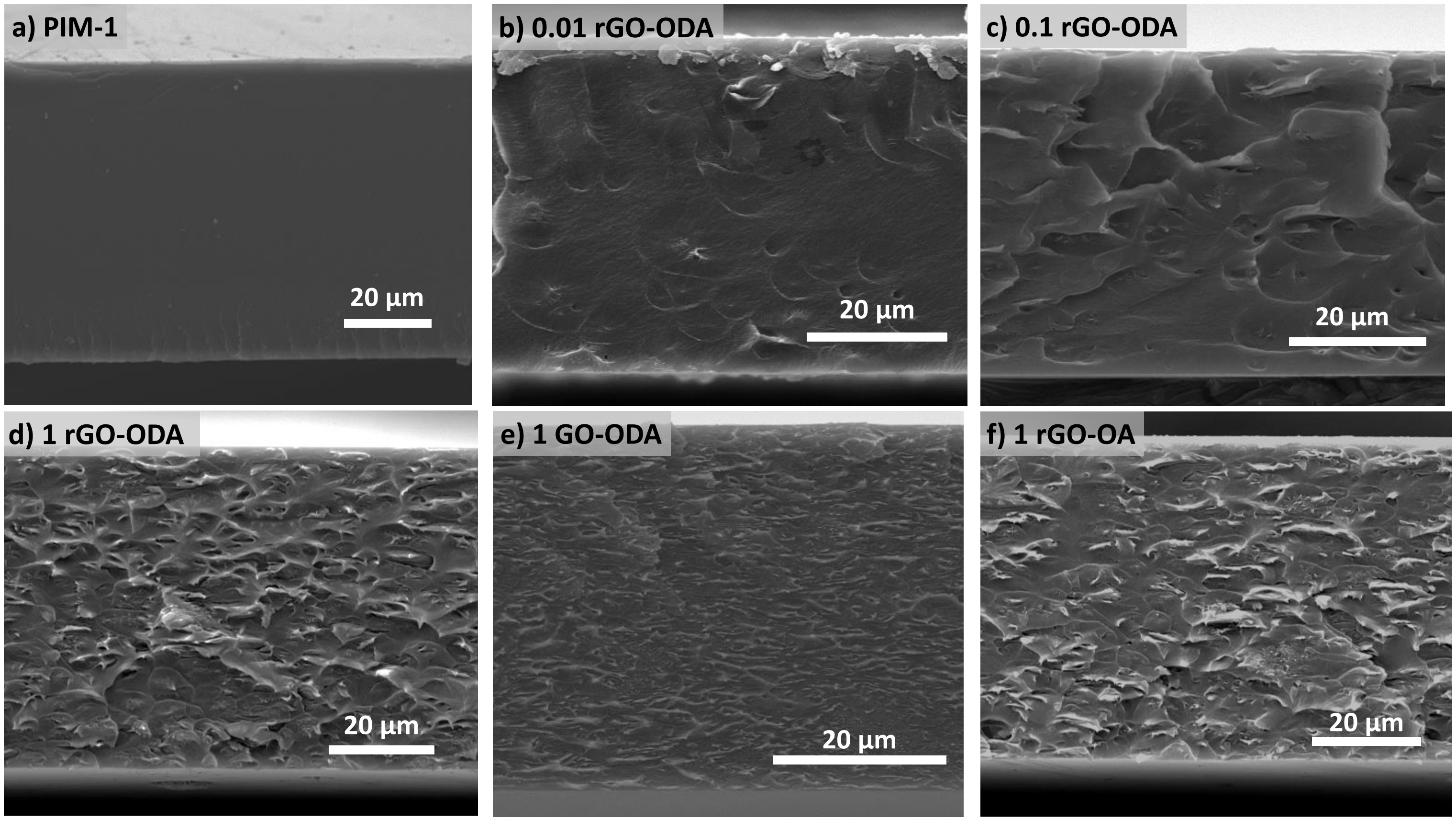
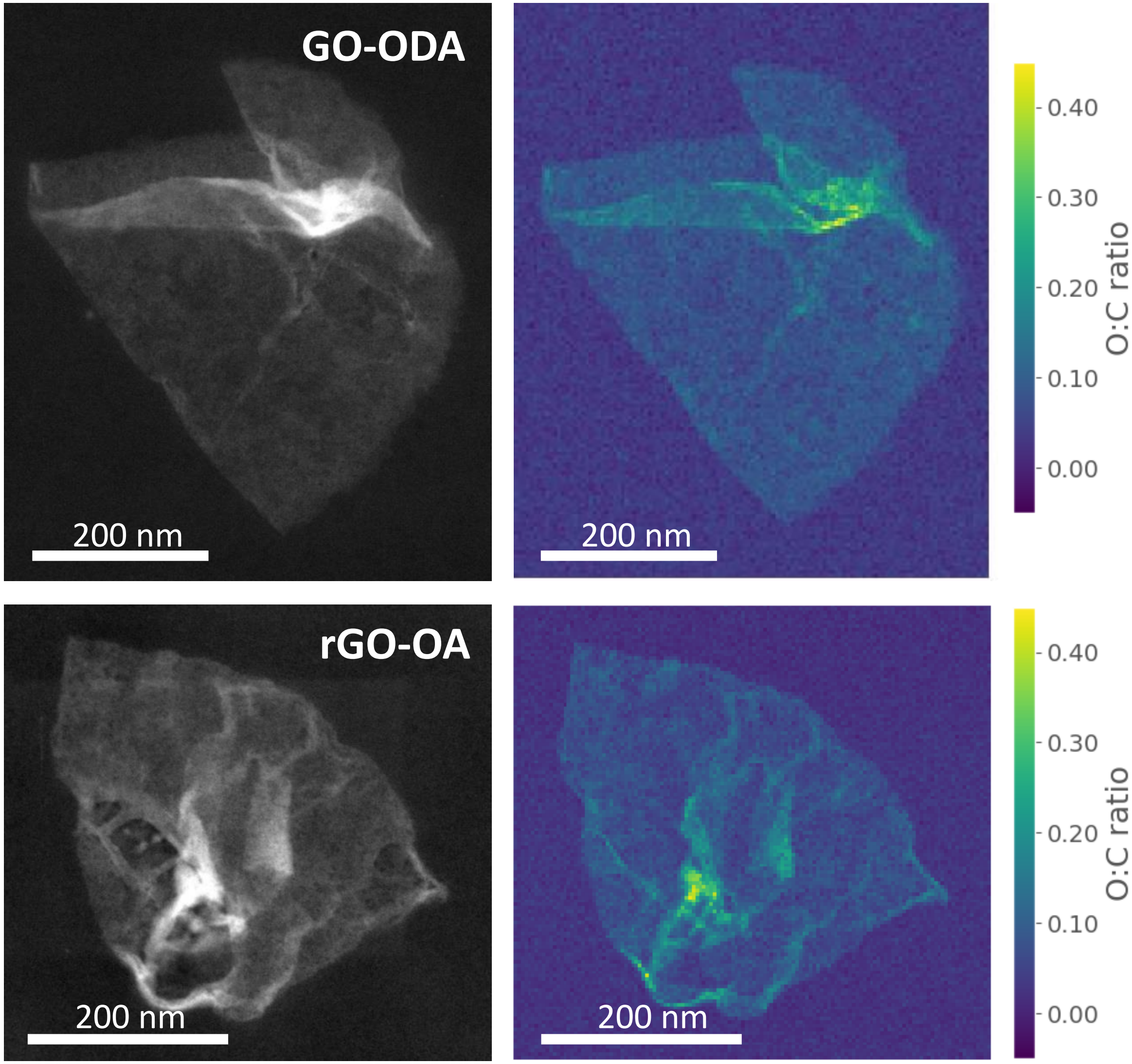
Membrane code	Filler	wt% of filler Values from the preparation of casting solutions	wt% of filler Values from UV of re-dissolved membranes *	Membrane Thickness (μm)*
PIM-1	-	-	-	60 ± 9.1
0.01GO-ODA	GO-ODA	0.01	0.040 ± 0.008	54 ± 6.5
0.1GO-ODA		0.1	0.197 ± 0.024	65 ± 4.2
0.5GO-ODA		0.5	0.601 ± 0.045	57 ± 2.2
1GO-ODA		1	1.340 ± 0.316	51 ± 8.8
0.01rGO-ODA	rGO-ODA	0.01	0.018 ± 0.003	59 ± 6.2
0.1 rGO-ODA		0.1	0.065 ± 0.012	56 ± 2.4
0.5rGO-ODA		0.5	0.316 ± 0.078	68 ± 7.6
1rGO-ODA		1	0.704 ± 0.207	52 ± 6.9
0.01rGO-OA	rGO-OA	0.01	0.031 ± 0.006	48 ± 3.9
0.1rGO-OA		0.1	0.125 ± 0.094	51 ± 2.1
0.5rGO-OA		0.5	0.487 ± 0.085	54 ± 6.3
1rGO-OA		1	0.972 ± 0.097	59 ± 6.1

(*) Average of 10 measurements with a screw gauge in different areas of the membrane.

Membrane characterization: SEM



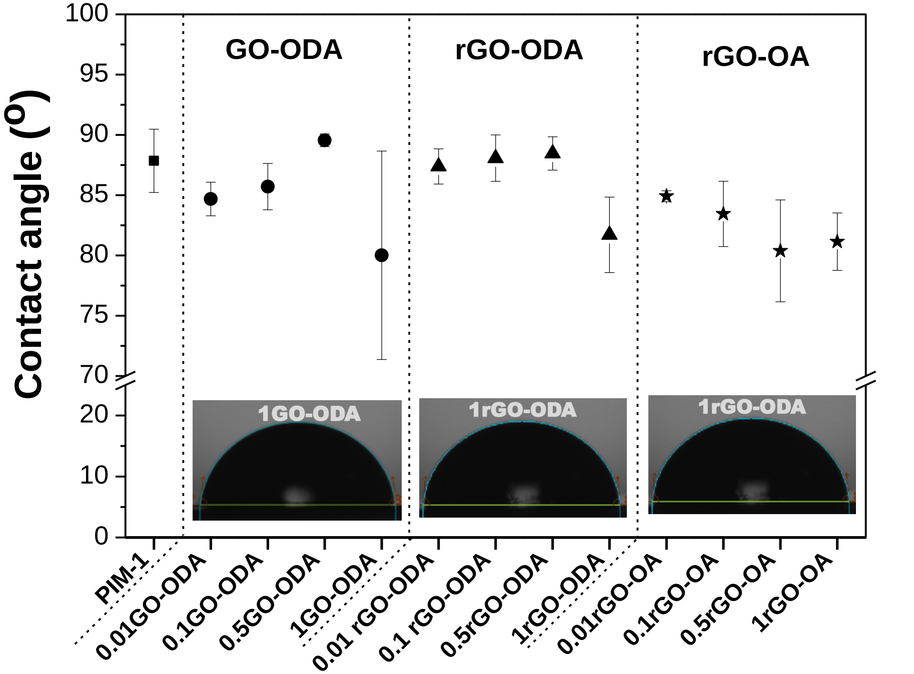
Membrane characterization: STEM



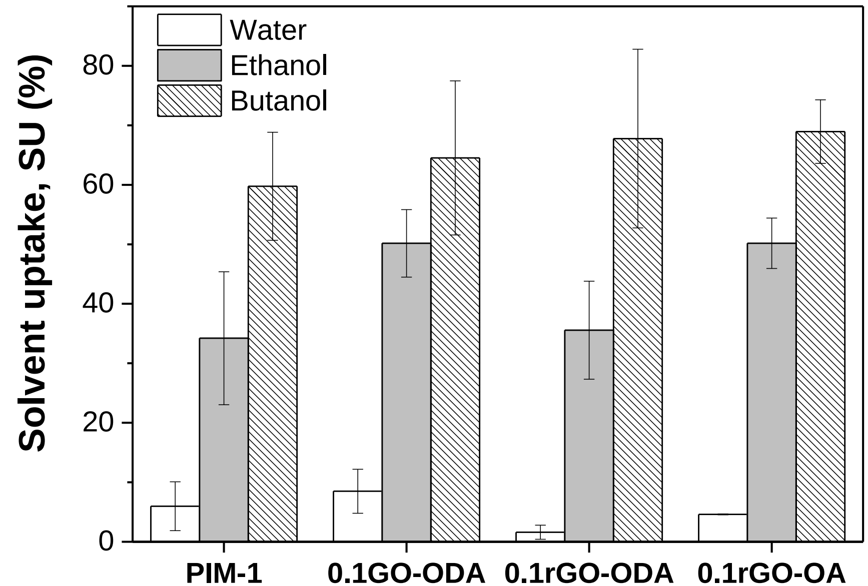
- Presence of single-layer flakes of GO-ODA and rGO-OA in the polymeric matrices
- O:C ratio mapping → features correspond to alkylamine - functionalized GO flakes

Membrane characterization

Contact angle



Solvent uptake



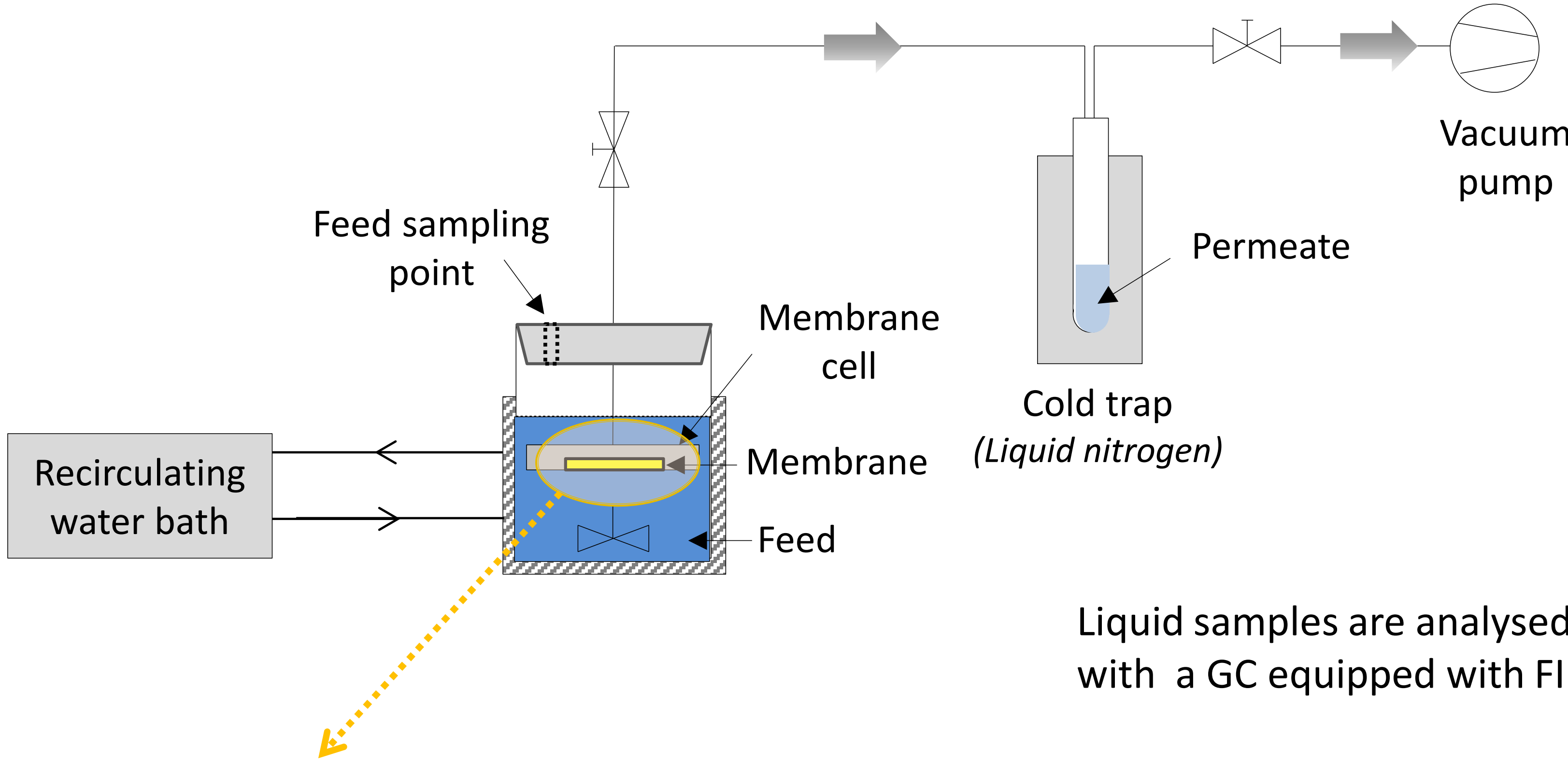
$$SU = \frac{m_f - m_i}{m_i} \times 100\%$$

3 days

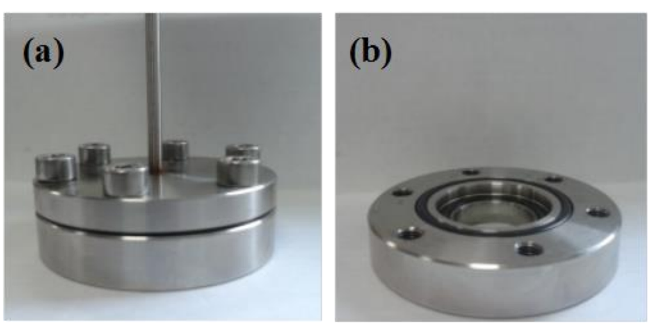
- All values for water ranged from 80 to 90˚→ addition of graphene-like fillers do not change significantly the surface properties
- ethanol contact angles 9.8° - 15.4° (13° for PIM-1)
- butanol contact angles 7.6° - 9.8° (9° for PIM-1)

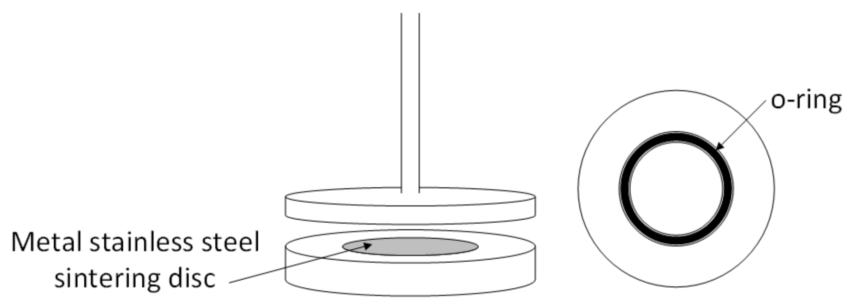
- All the membranes show preferential sorption butanol > ethanol > water,
- Graphene-based fillers improve in all cases the sorption towards alcohols
- Chemically reduced samples hinder the sorption of water

Pervaporation set-up



Liquid samples are analysed with a GC equipped with FID





PV performance of MMMs

Experiment conditions

Feed composition: ~5wt% EtOH/BtOH in H_2O

Feed temperature: 65 ^oC

Downstream pressure: 10 mbar

Effective membrane area: 2.5 x 10^{-4} m^2

Flux, *J*

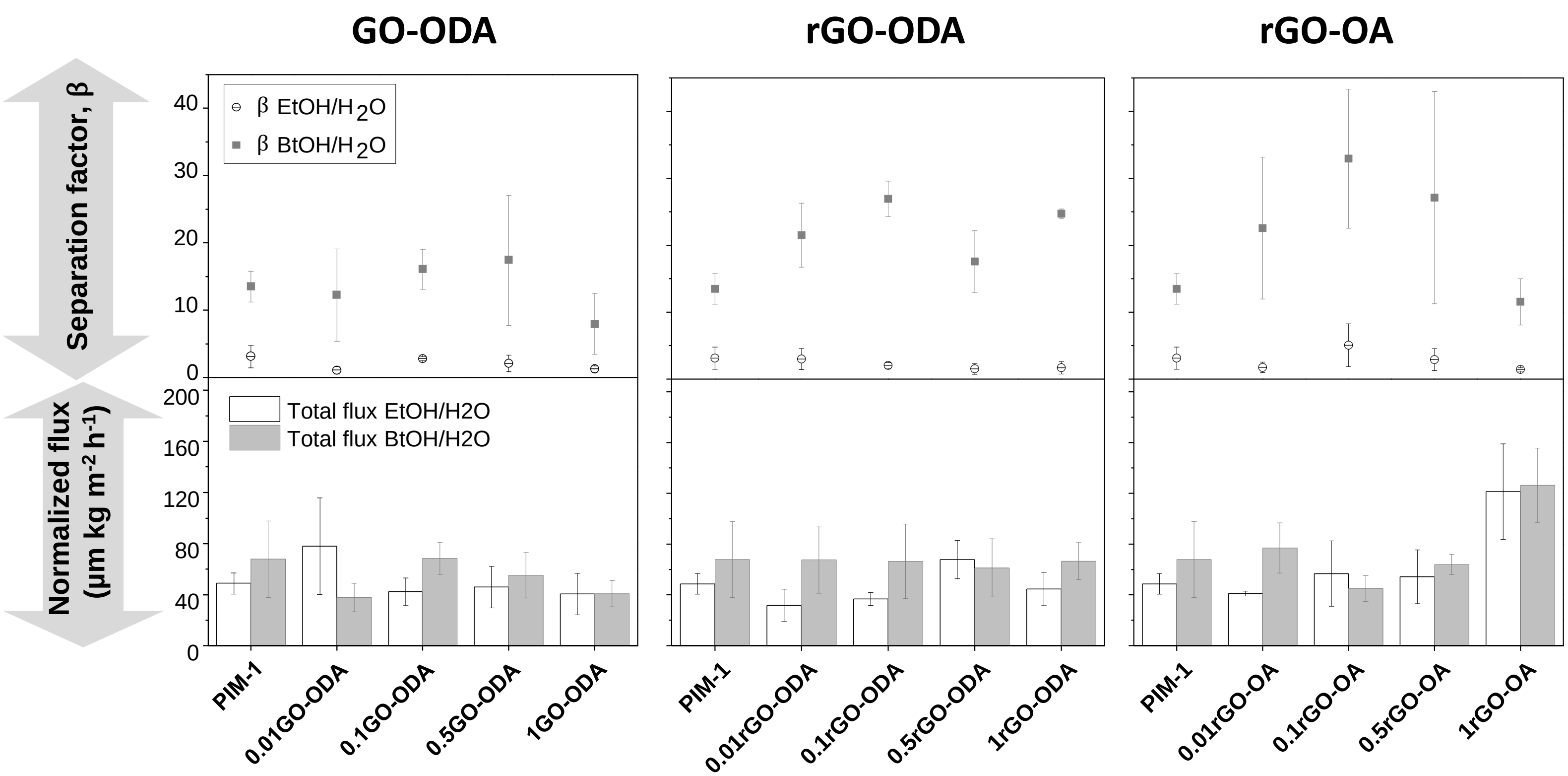
$$J = \frac{m}{A\,t}$$

m: weight of the permeate (kg)
A: effective area of the membrane (m^2)
t: permeate collection time (*h*)

Separation factor, β

$$\beta = \frac{Y/(1-Y)}{X/(1-X)}$$

Y: mole fraction of the alcohol in the permeate
X: mole fraction of the alcohol in the feed side



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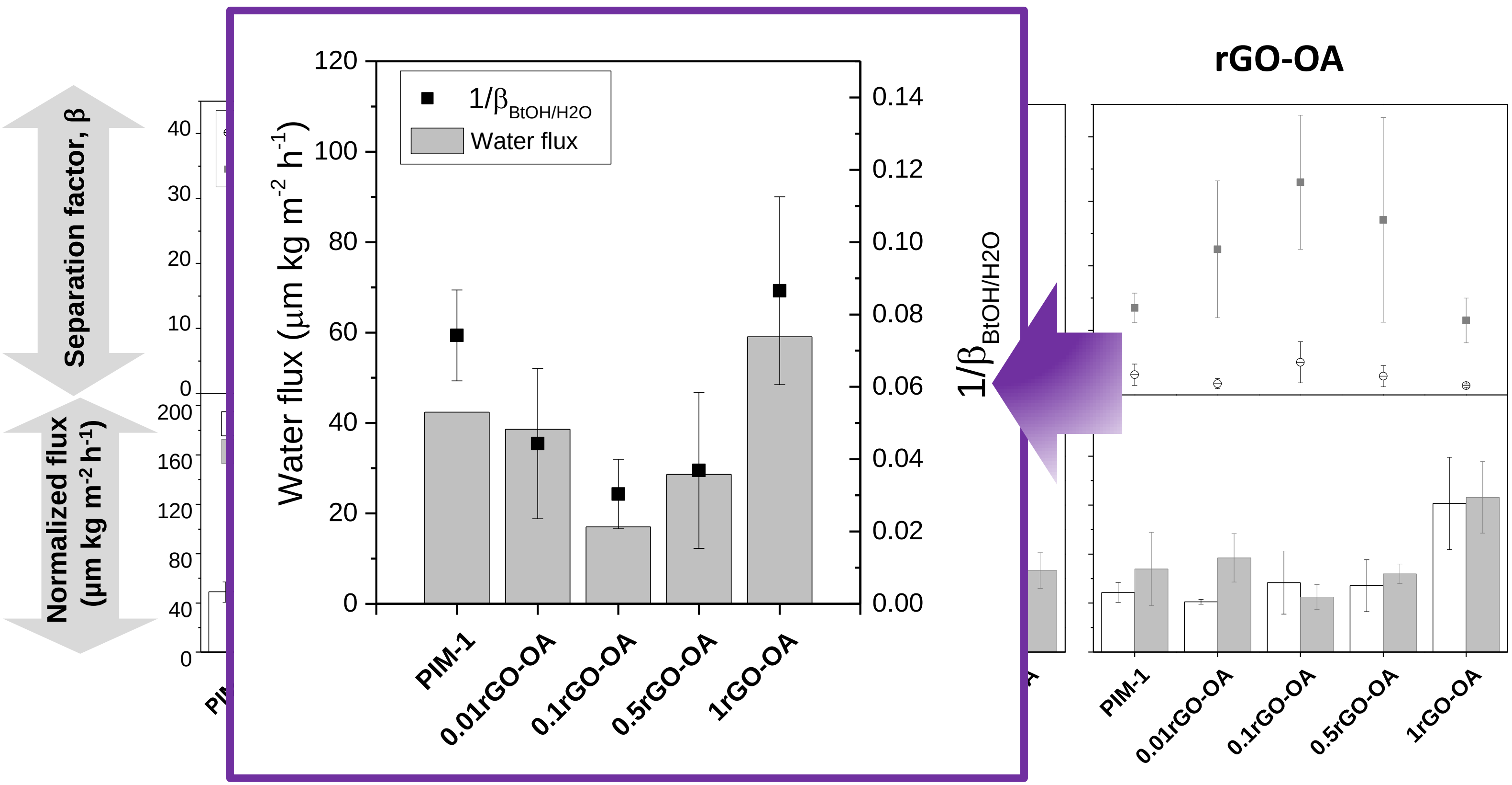
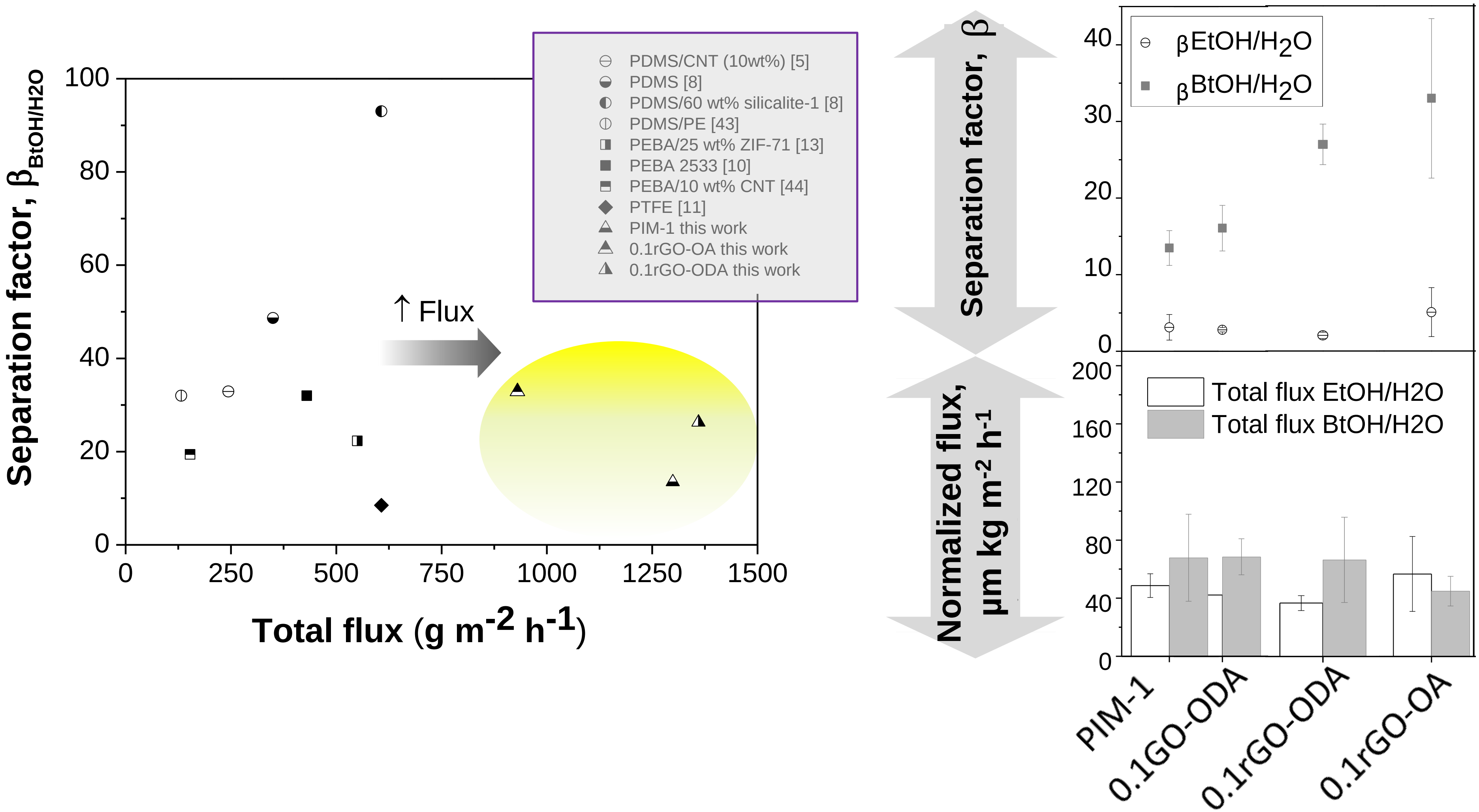


Comparison with reported values



Conclusions

i. Alkylamine-functionalized GO and rGO (GO-ODA, rGO-ODA, rGO-OA that could be dispersed in chloroform was prepared.

ii. Free-standing MMMs were prepared with PIM-1 and these graphene-like materials.

iii. The MMMs were tested for ethanol and butanol recovery from water via pervaporation

iv. 0.1 wt% of filler showed the highest improvement in selectivity towards butanol

Acknowledgments

Molecular separations
(School of Chem. Eng.)
&
Nano-fuctional materials
(School of Materials)

Prof Budd's group
School of Chemistry

Dr Haigh and Dr Prestat
TEM experts