Preparation of Functional Membranes

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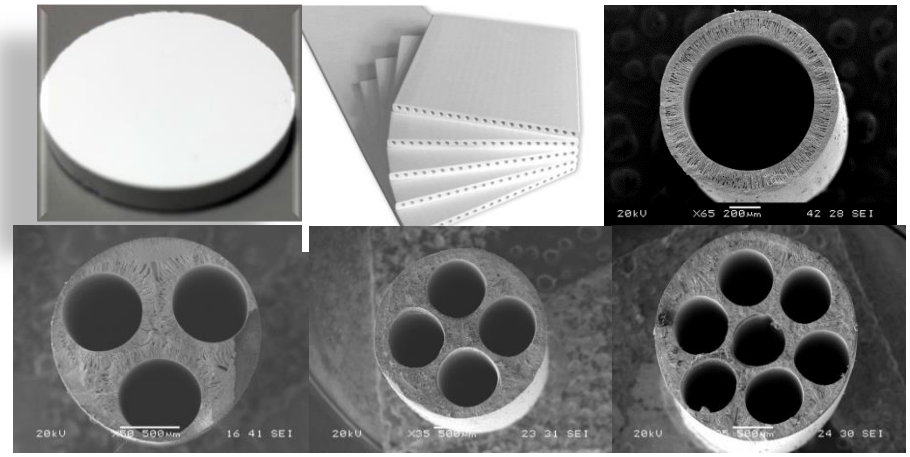
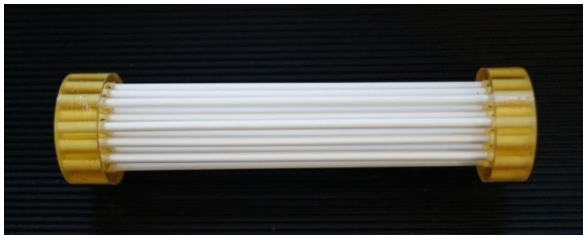
Inorganic membranes with a variety of geometries

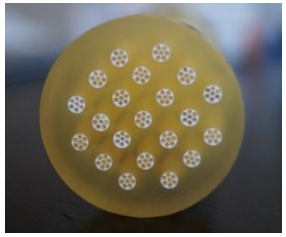
❖ Geometries

- Disk
- Flat-sheet
- Hollow fibre
- Multi-channels



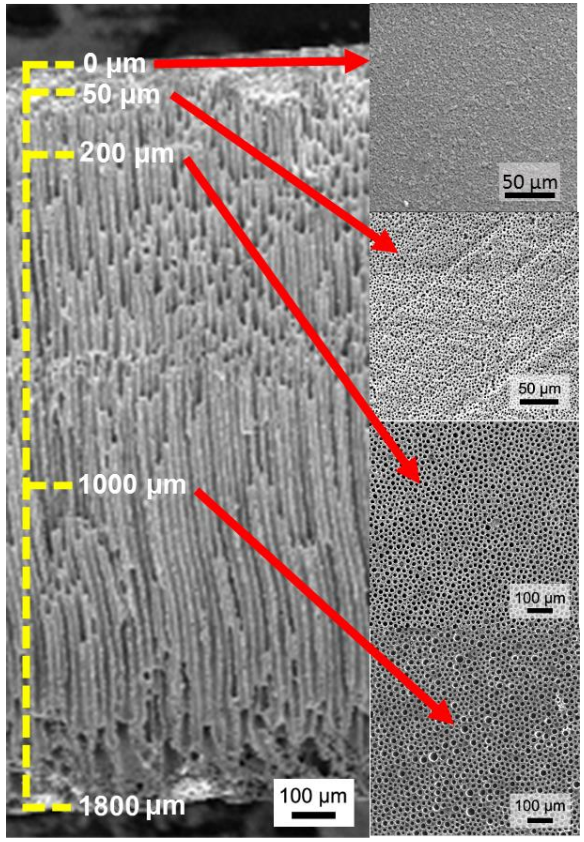
❖ From membranes to modules





From geometry to morphology control

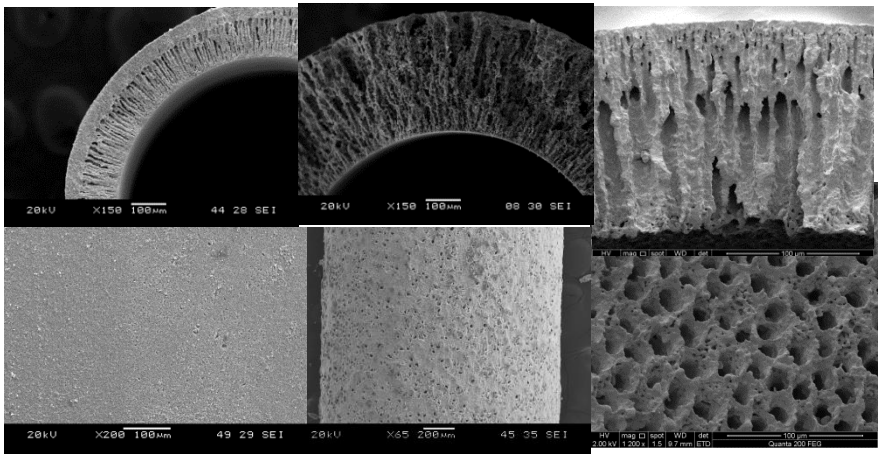
❖ Membrane cross-sectional structure design



Hierarchical structure of micro-channels in an flat-sheet alumina membrane

Interfacial instability

- Rayleigh-Taylor,
- Viscous fingering,
- Marangoni effect

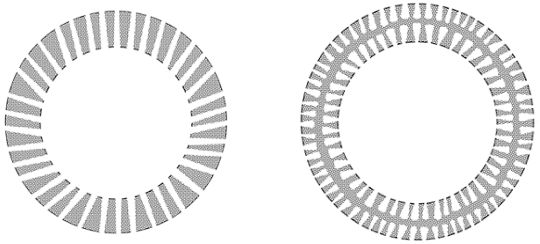


Micro-channels sandwiched by inner and outer separation layers

Micro-channels open at the outer surface

Micro-channels open at the inner surface

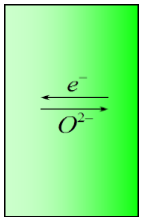
And other morphologies…

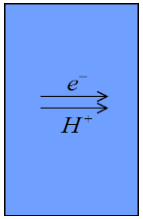


The fabrication technique is quite versatile and can be used for almost all the inorganic materials:

- Functional ceramics
- Engineering ceramics
- Metals

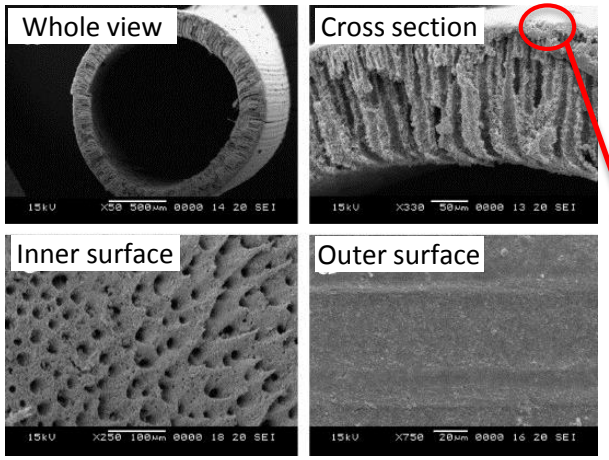
Dense functional ceramic membranes



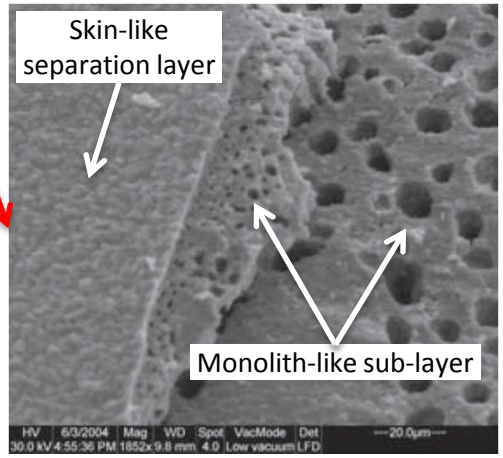


- Mixed ionic–electronic conducting (MIEC) membranes for oxygen separation
  - *Perovskite type materials:* $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, *etc.*
  - *Dual-phase composite materials:* $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ - $La_{0.8}Sr_{0.2}MnO_{3-\delta}$, $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ - $La_{0.7}Sr_{0.3}MnO_{3-\delta}$, *etc.*
- Mixed proton–electronic conducting membranes for hydrogen separation
  - *Perovskite type materials:* $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$, $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ etc.
  - *Dual-phase composite materials:* $SrZrO_{3-\delta}$ - $SrFeO_{3-\delta}$, $La_{27}W_{3.5}Mo_{1.5}O_{55.5-\delta}$ - $La_{0.87}Sr_{0.13}CrO_{3-\delta}$, *etc.*

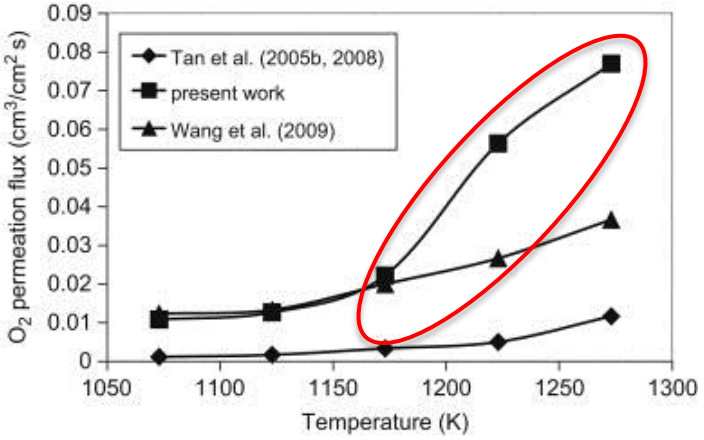
Morphology design leads jumps of the performance



SEM images of micro-structured LSCF hollow fibre membranes



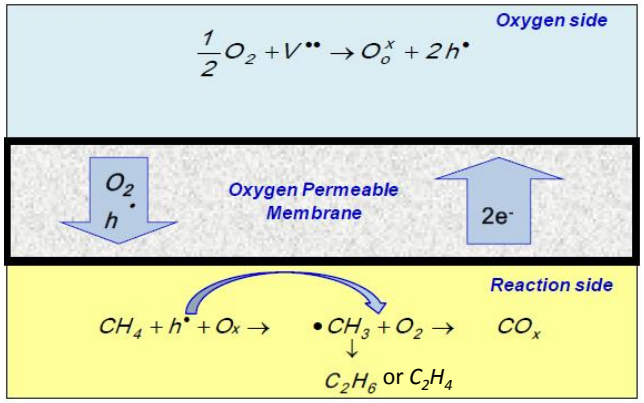
Unique gradually changed structure

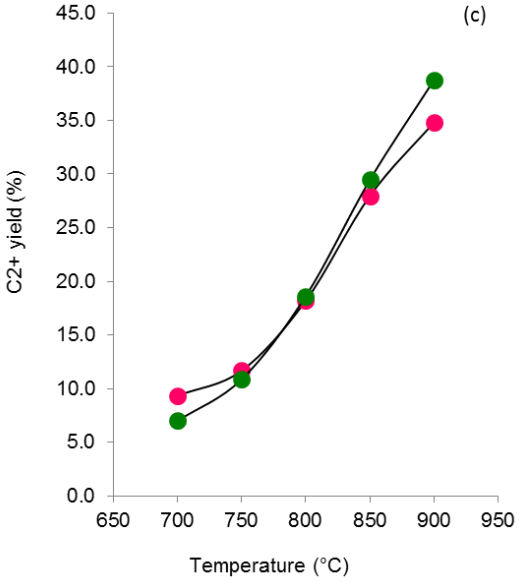


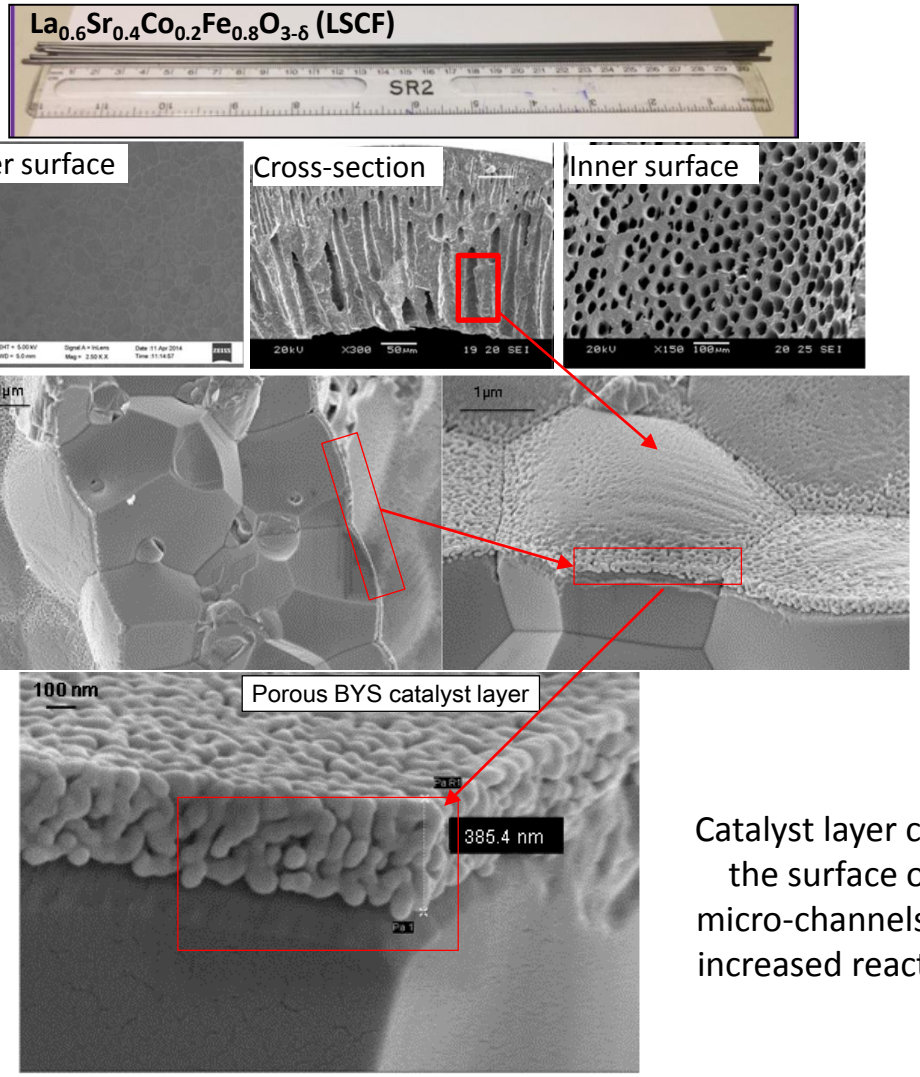
Very much improved oxygen permeation flux

Ceramic membrane reactors: multi-functionality

Oxidative Coupling of Methane (OCM)







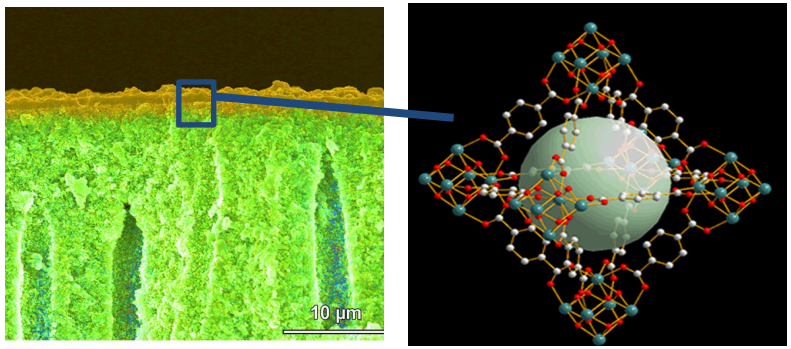
Catalyst layer coated on the surface of open micro-channels offering increased reaction sites

Engineering ceramic membranes: Al_2O_3, Yttrium stabilised zirconia (YSZ), SiC etc.

1. Microfiltration & Ultrafiltration:

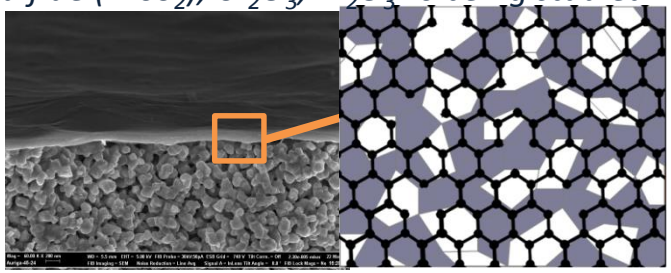
- 0.02-1 µm pore size suitable for most MF/UF applications;
- high permeation flux;
- low fouling tendency
- high temperature and high pressure use

2. As a substrate for a variety of separation layers

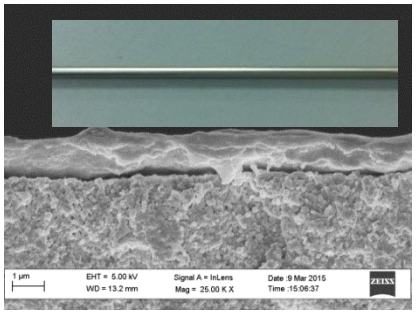


a) UiO-66, Zirconium Metal-Organic Framework (MOF) membrane for organic solvent dehydration and sea water desalination, Liu, Xinlei, et al. *JACS* , 137 (2015) 6999.

***Other 2-D materials such as Molybdenum disulfide (MoS_2), Cr_2O_3, Al_2O_3 is being studied*



(b) Supported graphene/graphene oxide membrane for for organic solvent and water permeation , Aba et.al.,JMS , 484(2015)87

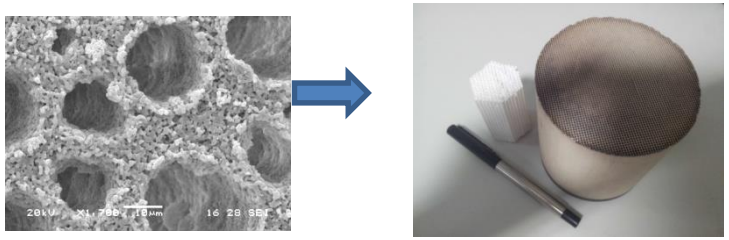


(c) Plating of Pd and Nickel membrane for hydrogen separation

3. Catalytic convertor substrate

- 60% reduction in catalyst loading
- 50% reduction in catalyst ageing
- 40 – 70% reduction in pressure drop
- 50% reduction in catalytic converter volume

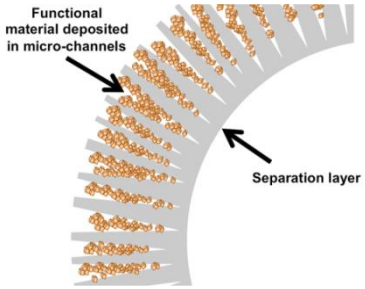
Coating of three-way catalysts in micro-channels for emission control

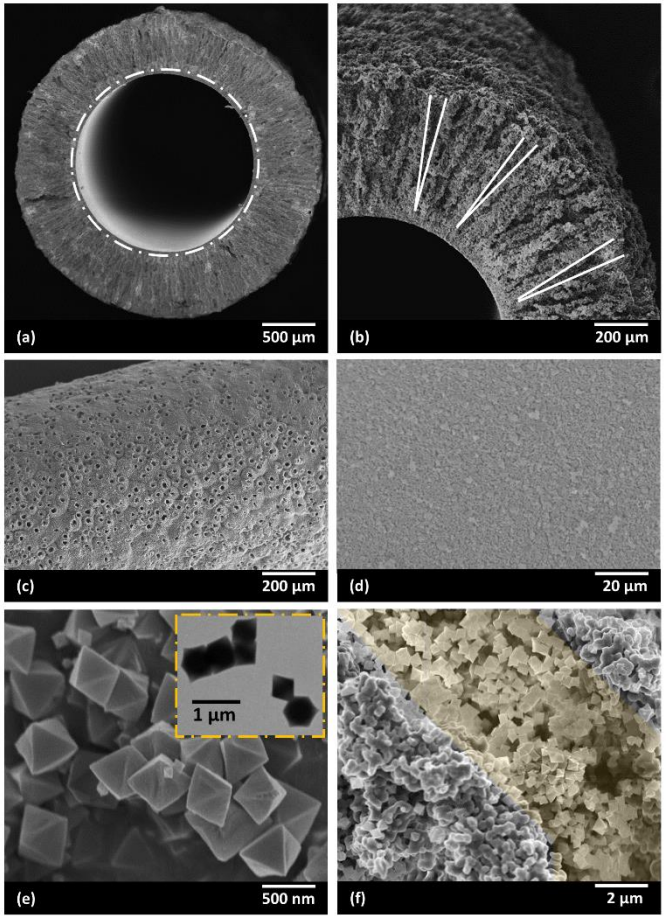


Led to a spin-out company **MicroTech Ceramics Limited**

Multifunctional membranes: the incorporation of functional materials

- Incorporation of catalysts and adsorbents into membranes: Separation/filtration, adsorption or reaction achieved in one step

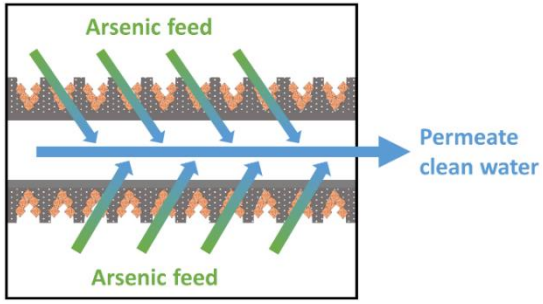




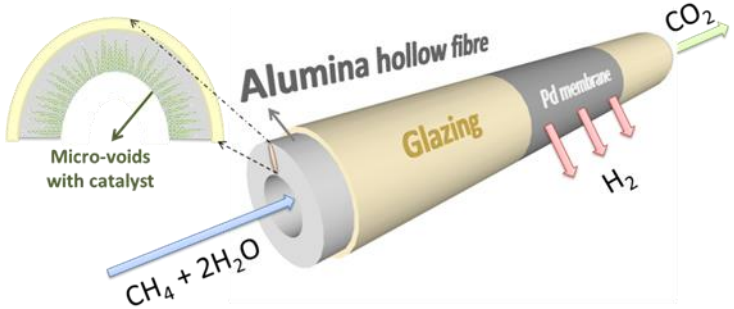
Ceramic hollow fibre membrane embedded with UiO-66 particle for arsenic removal

*Wang, C. et al., *Chem. Commun.* **2016,** *52* (57), 8869-8872.

1. Simultaneous microfiltration and arsenic removal

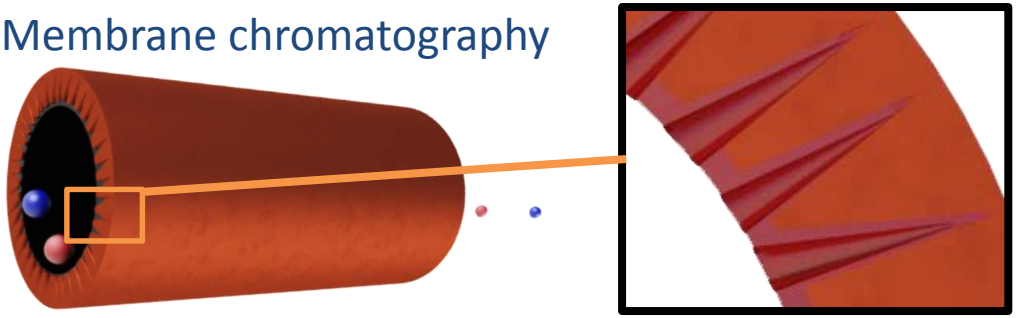


2. Hydrogen permeation and methane conversion



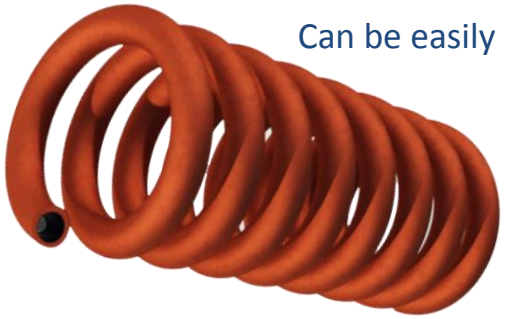
Metallic hollow fibres

❖ Membrane chromatography



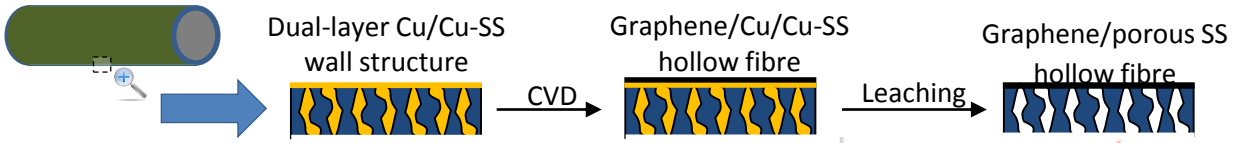
Copper hollow fibre with open micro-channels offer increased surface area

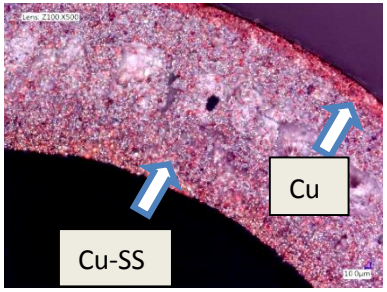
Coated with GC stationary phase



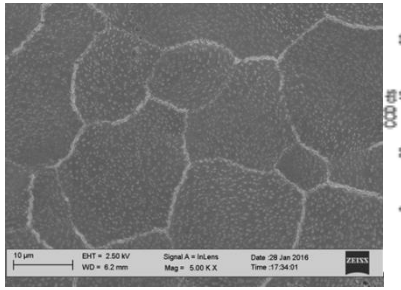
Can be easily coiled up

❖ Supported graphene membranes

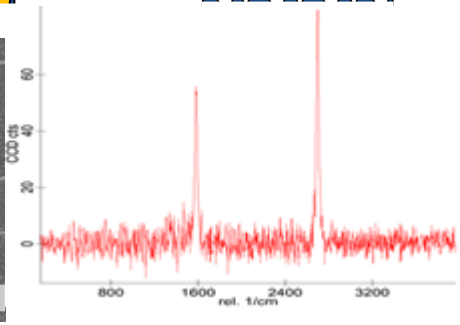




Dual-layer fibre



Dense copper layer surface



Raman Spectrum shows continuous graphene after CVD

The New capillary GC column

- Negligible pressure drop
- Surface area/volumn can be 15 times higher than normal capillary columns with same diameter
- Accordingly higher stationary phase loading , resulting in better separation efficiency
- Possibility to separate gas pairs unachievable by normal capillary columns

Green manufacturing process for high performance membranes

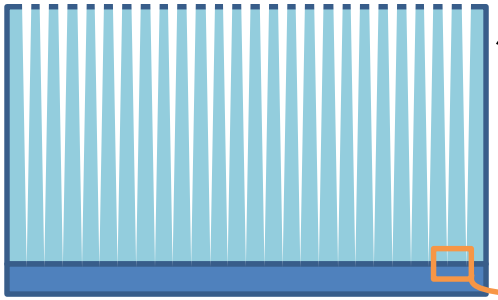
❖ Combined Crystallisation and Diffusion (CCD) Method: An versatile membrane fabrication technique

Step 1: Casting

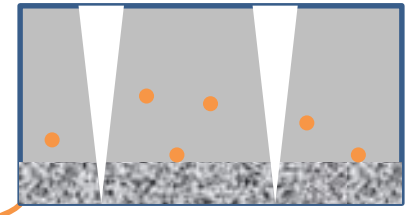
Step 2: Transfer onto a cold plate

Step 3: Remove solvent in leaching medium

***Zero discharge achievable when a volatile liquid is used as the leaching medium.*



Solvent nucleation and crystallisation

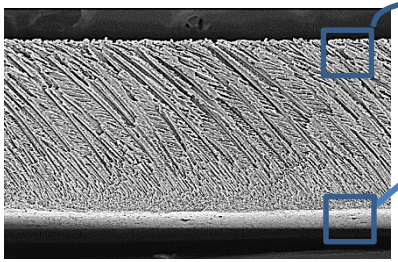


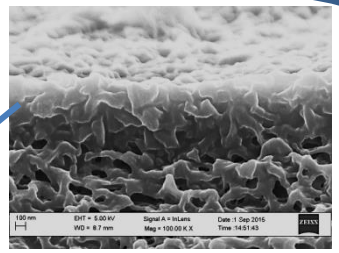
Formation of separation layer controlled by kinetics

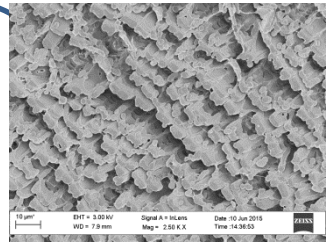
1. Solvent nucleation
2. Phase separation
3. Polymer diffusion

Unidirectional cooling from bottom

❖ A different PVDF membrane achieved







Water flux one order of magnitude higher than commercial PVDF membranes with similar pore size,

*Wang, et al , *Nat. Commun.* **2016,** *7*, 12804.

Acknowledgement

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