Supplementary information

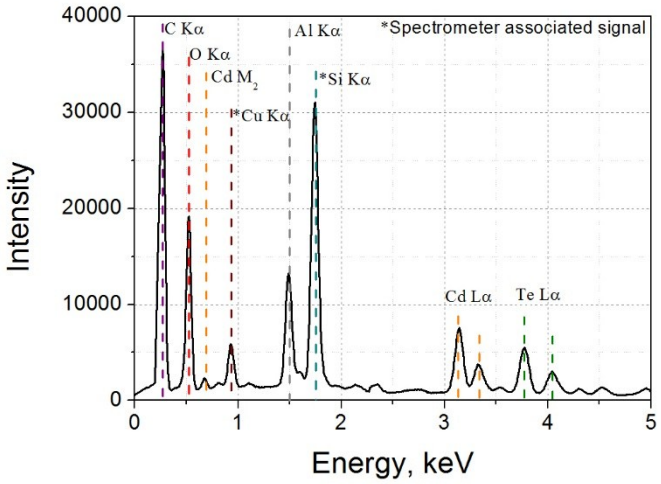
Labyrinthine transport of hydrocarbons through the grafted laminar CdTe nanosheet membranes.

Dmitrii Petukhov[a,b], Ilia Sadilov[*a], Roman Vasiliev[a,b], Larisa Kozina[b], Andrei Eliseev[a]

[a] - Department of Materials Science, Lomonosov Moscow State University, Moscow 119991 Leninskie gory 1-73, Russia

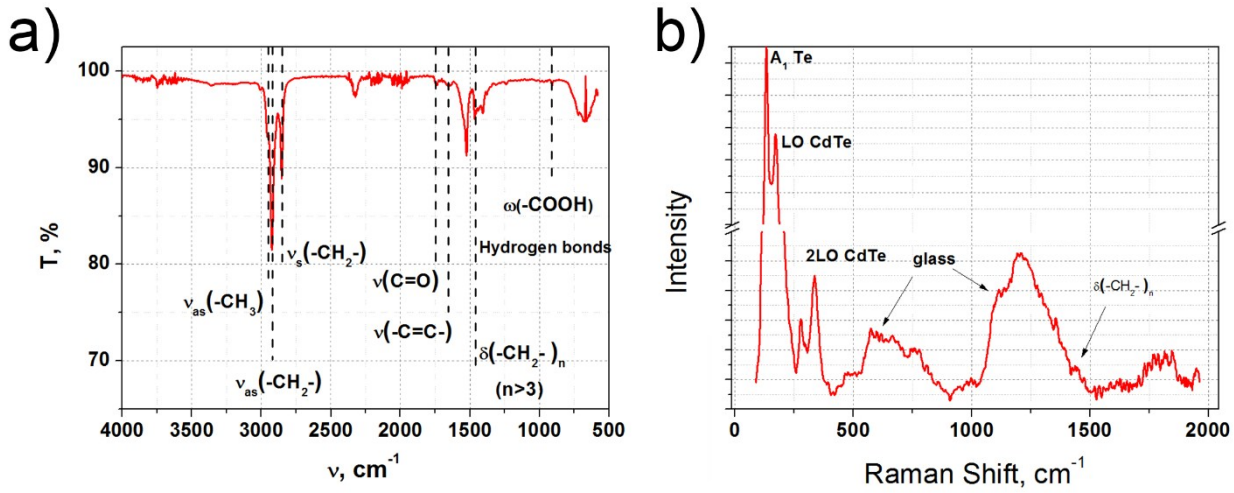
[b] - Department of Chemistry, Lomonosov Moscow State University, Moscow 119991 Leninskie gory 1-3, Russia

Corresponding author Ilia Sadilov, e-mail: ilsadilov@yandex.ru

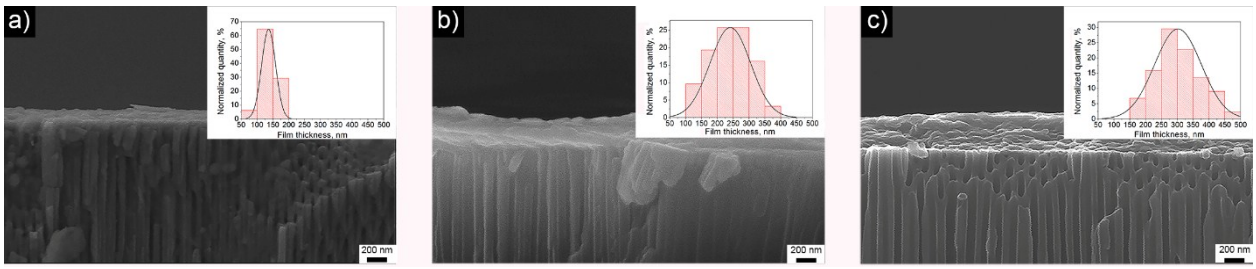


Element	Line Type	At. %	At. % Sigma
C	K series	66.99	0.22
O	K series	19.48	0.15
Al	K series	4.13	0.02
Cd	L series	5.14	0.02
Te	L series	4.27	0.02

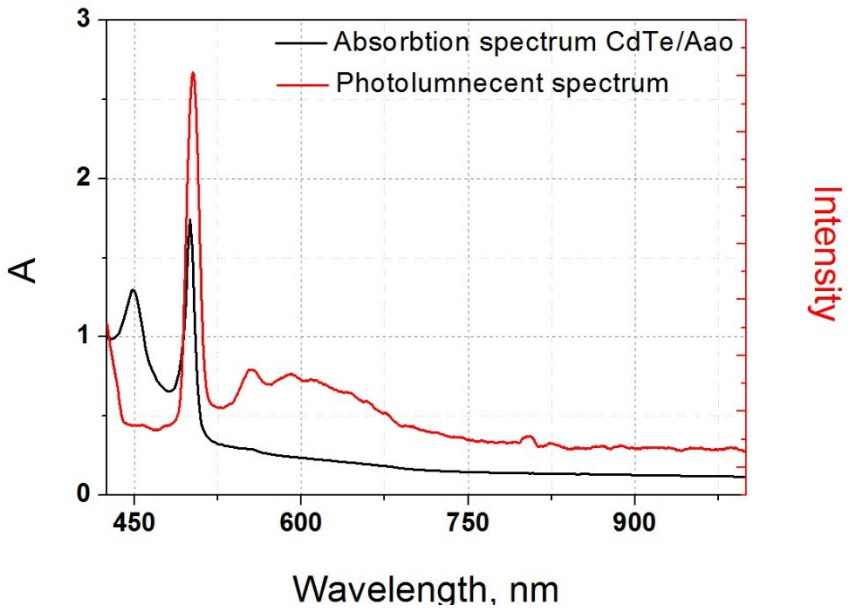
SI 1: Results of CdTe nanosheets EDX characterization



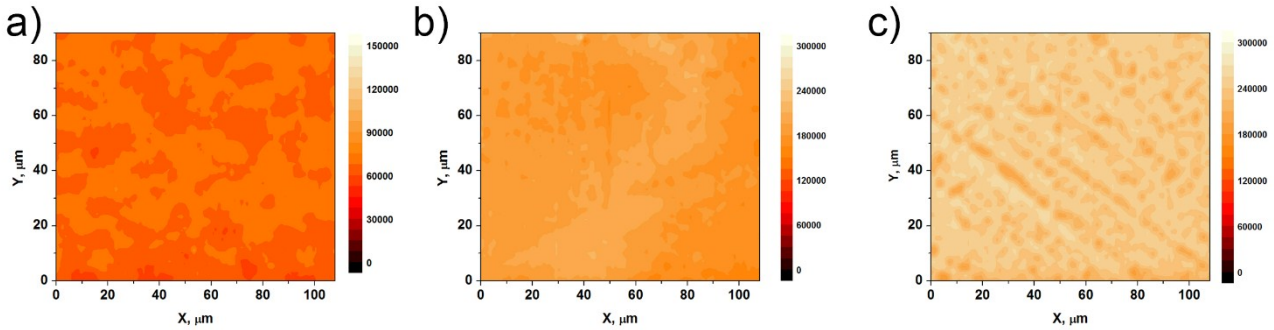
SI 2. Results of CdTe nanosheets characterization with IR (a) and Raman spectroscopy (b)



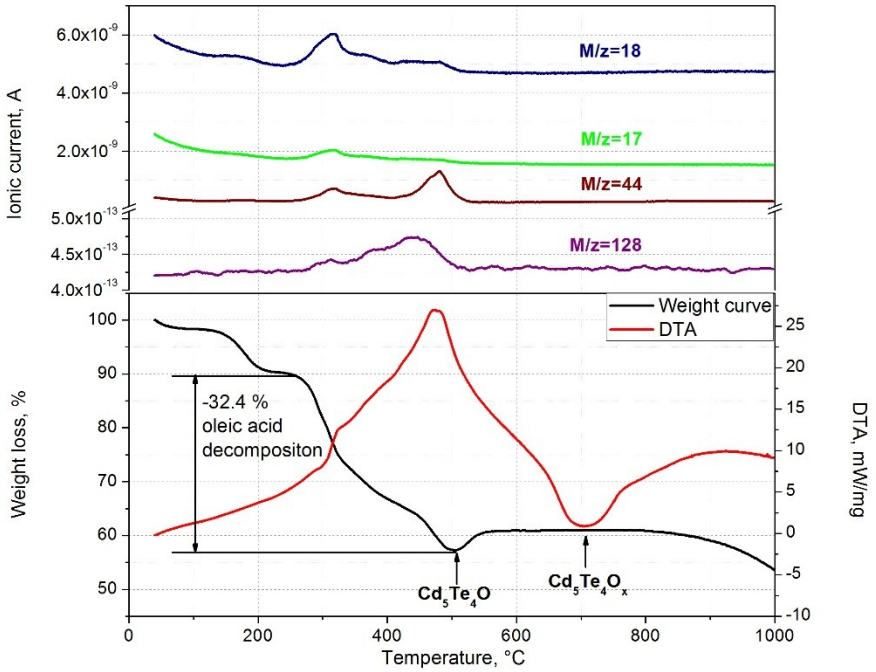
SI 3. Cross sectional SEM micrographs of CdTe/AAO membranes



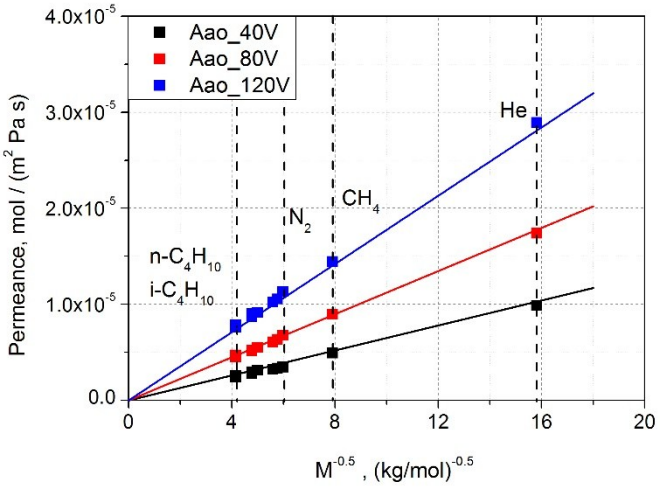
SI 4: Optical absorption and photo luminescent spectra of CdTe nanosheets.



SI 5. Results of photo luminescent mapping of membranes selective layer (a) CdTe/AAO40V, (b) CdTe/AAO80V, (c) CdTe/AAO120V.



SI6: Thermal analysis results and MS-signal for mass number 18, 17 (H_2O), 44 (CO_2) and 128 (Te) for CdTe nanoflakes. This experiment was performed in air by heating to 1000 °C at 5 °C/min heating rate.



SI7. Permeance of initial AAO supports vs inverse square root of gas molecular weight. All measurements were performed at 25°C.

SI 8. Calculation of selective layer permeance

Permeance (F) of asymmetric membrane depends both on permeance of selective ($F_{selective}$) and supporting layer ($F_{supporting}$) according to following equation [7]:

$$\frac{1}{F} = \frac{1}{F_{selective}} + \frac{1}{F_{supporting}} \quad (8.1)$$

Taking into account permeance of AAO support the permeance of selective layer can be calculated as:

$$F_{selective} = \frac{1}{\frac{1}{F} - \frac{1}{F_{supporting}}} \quad (8.2)$$

Permeability of selective layer can be calculated taking into account thickness of selective layer:

$$P_{selective} = F_{selective} \cdot l \quad (8.3)$$

SI 9: Derivable diffusion coefficients for different gases in grafted Vycor glasses [1] and grafted AAO membranes [2], taking into account sorption coefficients measured in the current work and the thickness of membrane given in [1,2].

Gas	Grafted Vycor glass membrane		Grafted AAO membrane	
	Permeability x10^{12}, mol·m/(m^2·Pa·s)	D x10^9, m^2/s	Permeability x10^{12}, mol·m/(m^2·Pa·s)	D x10^9, m^2/s
N_2	4.7	7.0	0.04	0.57
O_2			0.08	1.07
CH_4			0.12	0.82
C_2H_6	35	13.9	0.20	0.81
CO_2	38	42.5	0.43	4.78
C_3H_8			0.97	2.02
i-C_4H_{10}	105	13.7	1.26	1.65
n-C_4H_{10}	241	20.7	2.33	2.00

SI 10: Theoretical calculation of liquid butane permeance in CdTe nanosheets layer

Liquid flux through the slit-like pore can be calculated using Poiseuille equation:

$$J = \frac{h^3}{12\mu} \cdot \frac{dP}{L} \tag{8.1}$$

where h – thickness of oleic acid layer available for diffusion (2.1 nm), μ – condensate viscosity, dP – pressure difference, L – diffusion length.

Diffusion length, concerning labyrinthine flow of condensate can be calculated as:

$$L = \frac{L_{av}}{4} \cdot \frac{l}{d_{int}} \tag{8.2}$$

where L_{av} – average lateral size of CdTe nanosheet (260 nm), d_{int} – interflake distance equal to 3.4 nm and l – selective layer thickness.

To obtain value of membrane permeance the equation (8.1) should be normalized to dP, available area for liquid flow (A) and multiplied on the total width of slits:

$$P = \frac{h^3}{12\mu} \cdot \frac{4}{L_{av}} \cdot \frac{d_{int}}{l} \cdot \left(L_{av}\frac{1}{L_{av}^{\,2}}\right)\left(L_{av}h\frac{1}{L_{av}^{\,2}}\right)^{-1} = \frac{h^2 d_{int}}{3\mu \cdot L_{av} \cdot l} \tag{8.3}$$

To convert the results calculated using eq. 8.3 from liquid volume to gas volume (STP) we should multiply the equation to factor $\frac{\rho V_m}{M_r}$

$$P = \frac{h^2 d_{int}}{3\mu \cdot L_{av} \cdot l}\frac{\rho V_m}{M_r} \tag{8.4}$$

Calculated permeance membrane on the assumption of butane liquid flow through the membrane is equal $7.5 \cdot 10^{-6}$ mol/(m^2·Pa·s).

SI 11: Theoretical calculation of activation energy of butane molecules hopping diffusion.

For estimation activation energy of butane diffusion, we can use the following equation describing molecules hopping diffusion:

$$J = \frac{L_{jump}}{L_{labirint}} \cdot N \cdot f_0 \cdot e^{-\frac{E_a}{kT}} \quad (9.1)$$

where L_{jump} – is an average jump length, $L_{labirint}$ – total traveling distance of molecule in selective layer, f_0 – frequency of butane molecule jump, N – number of molecules in selective layer, E_a – activation energy of diffusion.

$L_{labirint}$ can be calculated as:

$$L_{labirint} = \frac{L_{av}}{4} \cdot \frac{l}{d_{int}} \quad (9.2)$$

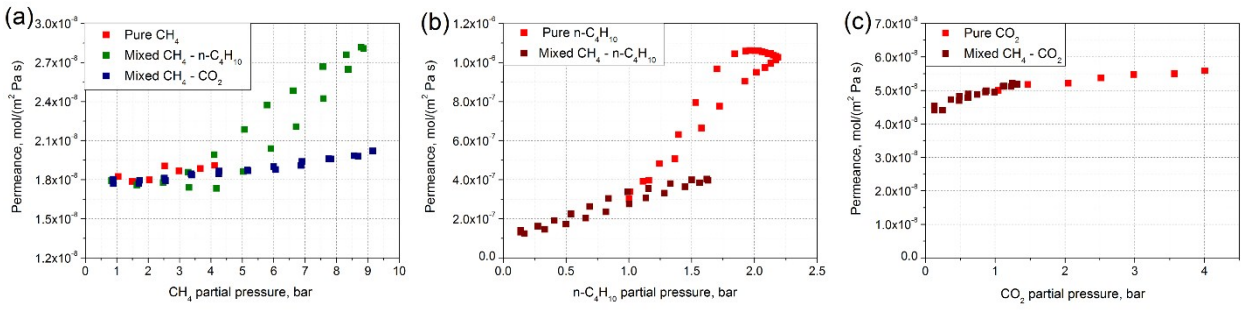
Number of molecules in selective layer can be estimated using sorption constant for required pressure and taking into account the volume of oleic layers:

$$N = h \cdot A \cdot \rho_{oleic} \cdot K_{sorption} \quad (9.3)$$

We unable to found the simulation of butane molecules diffusion in grafted layer, so we used the average values of molecule residence time in free volume of PDMS equal to 5 ps and the length of jump equal to 11 Å [3].

The calculated values of activation energy for butane molecule jump at different feed pressure conditions are listed in the following table:

Pressure difference, bar	Membrane permeance x10^7, mol/(m^2·Pa·s)	Sorption constant, mmol/g(grafted)	Activation energy, eV
1	3	1.3	0.32
1.25	4.8	1.5	0.31
1.5	7.9	2.0	0.30
1.71	9.7	3.8	0.30
2	11	6.9	0.31
2.18	10	13.5	0.31



SI 12. Permeance pure and mixed gases against partial pressure for methane (a), n-butane (b), carbon dioxide (c). Feed streams containing 85.5 vol. % CH_4 with 14.5 vol. % n-C_4H_{10} and 87.5 vol. % CH_4 with 12.5 vol. % CO_2. All measurements were performed at 25°C.

References

1 R. P. Singh *et al, Ind. Eng. Chem. Res.*, 2004, **43**, 3033–3040.

2 I. S. Sadilov *et al, Sep. Purif. Technol.*, 2019, **221**, 74–82.

3 S. G. Charati; S. A. Stern, *Macromolecules*, 1998, **31**, 5529–5535.