Electronic Supplementary Information (ESI) for

Efficient ^{3}He/^{4}He Separation in Nanoporours Graphenylene Membrane

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Supplementary Tables

Table S1. System energy and energy/atom verses k-points.

k-points	System energy (eV)	Energy/atom (eV)
1×1×1	-413.0437	-8.6051
3×3×1	-414.3121	-8.6315
5×5×1	-414.3124	-8.6315

Table S2. Energy per atom difference between graphene and graphenylene.

	Energy/atom (eV)
graphene	-9.2738
graphenelyne	-8.6315
Energy difference	0.6423

Table S3. Transition state vibrational frequencies for ^{3}He, ^{4}He and the difference between the frequencies. The zero-point energies difference are half the vibrational frequencies.

□Δ (^{3}He) (meV)	□Δ (^{4}He) (meV)	□Δ (^{3}He)-(^{4}He) (meV)
210.5992	210.5992	0.0000
210.5312	210.5311	0.0001
210.2975	210.2974	0.0001

208.8759	208.8759	0.0000
208.6827	208.6827	0.0000
208.5515	208.5515	0.0000
207.8171	207.8171	0.0000
207.5955	207.5955	0.0000
207.2371	207.2371	0.0000
206.9364	206.9364	0.0000
206.7971	206.7971	0.0000
206.7291	206.7290	0.0001
199.0110	199.0110	0.0000
198.8332	198.8332	0.0000
198.8174	198.8174	0.0000
192.7433	192.7433	0.0000
192.7184	192.7183	0.0000
192.4701	192.4701	0.0000
185.2159	185.2159	0.0000
185.1788	185.1787	0.0000
183.1009	183.1009	0.0000
182.9167	182.9167	0.0000
182.8712	182.8712	0.0000
160.4355	160.4355	0.0000
154.2546	154.2546	0.0000
154.0719	154.0719	0.0000
154.0467	154.0467	0.0000
152.6689	152.6689	0.0000
152.6171	152.6171	0.0000
152.3707	152.3705	0.0002
152.2768	152.2766	0.0002
152.2024	152.2024	0.0000
149.8707	149.8706	0.0001
149.8013	149.8012	0.0001
149.7141	149.7141	0.0000
148.9141	148.9141	0.0000
148.8541	148.8541	0.0000
148.6181	148.6181	0.0000
146.3959	146.3959	0.0000
146.2699	146.2699	0.0000
146.2121	146.2121	0.0000
145.6294	145.6294	0.0000
145.5991	145.5991	0.0000
144.1731	144.1731	0.0000
144.0702	144.0700	0.0002
144.0491	144.0489	0.0002

138.1652	138.1652	0.0000
137.1799	137.1799	0.0000
137.1517	137.1517	0.0000
127.7846	127.7846	0.0000
127.7533	127.7533	0.0000
127.7097	127.7097	0.0000
126.1894	126.1894	0.0000
124.8510	124.8510	0.0000
124.8199	124.8198	0.0001
124.7845	124.7844	0.0000
123.6283	123.6257	0.0026
123.5866	123.5859	0.0006
123.5582	123.5568	0.0014
113.7622	113.7622	0.0000
110.5870	110.5870	0.0000
110.5567	110.5567	0.0000
110.4977	110.4977	0.0000
108.8657	108.8657	0.0000
102.0575	102.0575	0.0000
102.0434	102.0434	0.0000
101.9944	101.9944	0.0000
99.4222	99.4222	0.0000
99.2298	99.2281	0.0017
99.1969	99.1955	0.0014
97.9326	97.9326	0.0000
97.9144	97.9144	0.0000
97.9020	97.9020	0.0000
95.6733	95.6733	0.0000
95.6494	95.6494	0.0000
95.6338	95.6338	0.0000
90.7078	90.7078	0.0000
90.6876	90.6876	0.0000
90.6835	90.6835	0.0000
90.6005	90.6005	0.0000
90.5922	90.5922	0.0000
90.4722	90.4722	0.0000
90.3461	90.3461	0.0000
90.3426	90.3426	0.0000
90.2188	90.2188	0.0000
84.7632	84.7632	0.0000
83.3209	83.3207	0.0002
83.2959	83.2951	0.0008
83.2613	83.2604	0.0009

74.7624	74.7624	0.0000
74.7434	74.7434	0.0000
74.6765	74.6765	0.0000
71.3825	71.3825	0.0000
71.3529	71.3529	0.0000
71.3103	71.3103	0.0000
68.3868	68.3868	0.0000
68.3564	68.3563	0.0000
67.6039	67.6039	0.0000
67.5865	67.5865	0.0000
63.5687	63.5685	0.0002
63.0737	63.0730	0.0007
63.0525	63.0519	0.0007
62.6102	62.6102	0.0000
62.5829	62.5829	0.0000
62.5821	62.5821	0.0000
59.7627	59.7627	0.0000
59.7582	59.7582	0.0000
59.7392	59.7392	0.0000
57.6155	57.6155	0.0000
57.5742	57.5742	0.0000
57.5483	57.5483	0.0000
57.4589	57.4585	0.0003
56.0860	56.0859	0.0001
56.0351	56.0351	0.0000
56.0245	56.0245	0.0001
55.3384	55.3384	0.0000
55.2999	55.2999	0.0000
55.2984	55.2984	0.0000
52.4995	52.2966	0.2029
52.4012	52.2666	0.1346
52.2476	52.2417	0.0059
45.4426	43.9734	1.4693
43.9734	43.9325	0.0409
43.9325	39.5430	4.3894
43.9156	38.1602	5.7554
37.9469	37.9469	0.0000
37.9144	37.9144	0.0000
37.8629	37.8628	0.0000
26.9061	26.9061	0.0000
26.8828	26.8828	0.0000
26.1755	26.1755	0.0000
23.1339	23.1339	0.0001

23.0703	23.0703	0.0000
22.5774	22.5775	-0.0001
22.5451	22.5451	0.0000
22.4591	22.4591	0.0000
22.4061	22.4060	0.0001
8.6194	8.6192	0.0002
8.3370	8.3370	0.0000
8.0883	8.0881	0.0002
7.8486	7.5133	0.3353
7.1764	7.1763	0.0001
6.8666	6.8344	0.0323
5.9670	5.4381	0.5289

Supplementary Methods

1. Deduction of energy-temperature-dependent transmission probability *p(E,T)*

According to Maxwell-Boltzmann distribution, the distribution of the molecular velocities at temperature *T* in one-dimension is given by:

$$p(v,T) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_B T}}$$

.

Therefore, the thermally weighted transmission can be obtained by

$$p(T) = \int p(v,T)t(\frac{1}{2}mv^2)dv = \int p(E,T)t(E)dE$$

,

where *t(E)* is the transmission probability as a function of kinetic energy as introduced in the main text.

As such, we can obtain:

$$\begin{aligned} p(E,T) &= p(v,T)\frac{dv}{dE} \\ &= \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{E}{k_B T}} \frac{1}{\sqrt{2Em}} \\ &= \left(\frac{1}{4\pi k_B TE}\right)^{1/2} e^{-\frac{E}{k_B T}} \end{aligned}$$

2. Deduction of collision frequency between helium and the membrane z_{coll}

According to the Maxwell-Boltzmann distribution,

$$z_{coll} = \rho \frac{\langle u \rangle}{4}$$

where ρ is the particle density, which for an ideal gas is $\rho = \frac{P}{k_B T}$, and $\langle u \rangle$ is the mean velocity, which is given according to Maxwell-Boltzmann distribution by $\langle u \rangle = \left(\frac{8 k_B T}{\pi m} \right)^{1/2}$.

Therefore,

$$z_{coll} = \frac{1}{4} \frac{P}{k_B T} \left(\frac{8 k_B T}{\pi m} \right)^{1/2} = \frac{P}{\sqrt{2 \pi m k_B T}}.$$

3. Deduction of equilibrium quantum sieving ^{3}He/^{4}He separation factor *r*

According to the works by Schrier [1,2], the separation factor obtained by the transition state theory is

$$r_{TST} = e^{-\left(\Delta\left(^3He\right) - \Delta\left(^4He\right)\right)\left(1/(k_B T_C) - 1/(k_B T_H)\right)}.$$

To incorporate quantum tunneling effects into transition state theory, a tunneling factor is included [3,4]

$$\kappa = \frac{p(T)}{p_{classic}}.$$

Here, the $p_{classic}$ is the thermally weighted classical transmission probability. For ^{3}He and ^{4}He, $p_{classic}$ have the same value.

Solving the steady-state condition after incorporating the tunneling factor leads to a multiplicative factor of

$$\frac{\kappa_{T_C,\,^3He}}{\kappa_{T_C,\,^4He}} \frac{\kappa_{T_H,\,^4He}}{\kappa_{T_H,\,^3He}} = \frac{p(T_C,\,^3He)}{p_{T_c,classic}} \frac{p_{T_c,classic}}{p(T_C,\,^4He)} \frac{p(T_H,\,^4He)}{p_{T_H,classic}} \frac{p_{T_H,classic}}{p(T_H,\,^4He)} = \frac{p(T_C,\,^3He)}{p(T_C,\,^4He)} \frac{p(T_H,\,^4He)}{p(T_H,\,^4He)}$$

Therefore, the separation factor incorporating quantum tunneling effects into transition state theory is

$$r = \frac{p(T_C,\,^3He)}{p(T_C,\,^4He)} \frac{p(T_H,\,^4He)}{p(T_H,\,^3He)} e^{-\left(\Delta\left(^3He\right) - \Delta\left(^4He\right)\right)\left(1/(k_B T_C) - 1/(k_B T_H)\right)}$$

For a thoroughly deduction of the transition state theory incorporating quantum tunneling effects, one can refer to Ref. 2 for more details.

Supplementary Data

1. Sample INCAR for CNEB

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SYSTEM =tranistion state search
  PREC = Normal
  ISTART = 0
  ICHARG = 2
  ENCUT = 500
  IMAGES = 15
  SPRING = -5
  ICHAIN = 0
  LCLIMB = T
  IOPT = 1

  NELM = 80
  NELMIN = 2
  NELMDL = -8
  EDIFF = 1.E-05
  LREAL = A
  ALGO = Normal
  GGA = PE
  EDIFFG = -0.01
  NSW = 500
  IBRION = 3
  ISIF = 2
  POTIM = 0
  ISMEAR = 0
  SIGMA = 0.05
  LPLANE = T
  NPAR = 4
  LWAVE = F
  LCHARG = F
  LVDW= T
```

2. POSCAR for the optimized structure of the (2×2) supercell of the graphenylene lattice

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graphenylene
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     11.7086630296943959      -6.7599997520446751       0.0000000000000000
      0.0000000000000000      13.5199995040893555       0.0000000000000000
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0.0000000000000000 0.0000000000000000 20.0000000000000000

C

48

Direct

0.4394738096164200	0.1630558608638050	0.4999999634103887
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0.3369442127928597	0.2764181315046825	0.4999997660498181
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0.2235819382796451	0.0605262291247432	0.4999999768848724
0.2235819477763685	0.1630558584851069	0.4999999611859707
0.0605261951450832	0.3369442596486696	0.4999999748733472
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0.0605261743201699	0.2235820096972049	0.4999999756341182
0.2764180870414476	0.4394739009778273	0.4999997302692520
0.2764180790311014	0.3369442631896167	0.4999997399350349
0.9394738341576000	0.1630558355313435	0.4999999949145391
0.8369441490187859	0.0605261399212542	0.4999999924926186
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0.5605260958266486	0.3369442582840509	0.4999997916686283
0.6630557213092112	0.4394738828296563	0.4999997959602638
0.6630557391747212	0.2235820166455313	0.4999999796797567
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0.4394738334267497	0.6630557688955514	0.4999997265069567
0.3369442216111000	0.5605261526674882	0.4999997210894307
0.3369442015315531	0.7764180331385176	0.4999999749500219
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0.7764179639762773	0.9394737953626914	0.4999999775909032
0.7764179573970708	0.8369441572003160	0.4999999591192790

Supplementary References

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