

Supporting Information:

Graphdiyne: a versatile nanomaterial for electronics and hydrogen purification

Yan Jiao,^{ab} Aijun Du,^{*a} Marlies Hankel,^a Zhonghua Zhu,^{*b} Victor Rudolph^b and Sean C. Smith^{*a}

^a Centre for Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, QLD 4072, Brisbane, Australia.

^b School of Chemical Engineering, The University of Queensland, QLD 4072, Brisbane, Australia.

Computational Details

Electronic structure calculation:

The electronic structure of graphdiyne was computed by the plane-wave basis VASP code¹ implementing the projector augmented wave method². The calculations used the hybrid exchange-correlation functional HSE06³ which is able to predict experimentally measured band gaps with high accuracy.

Gas transmission calculation on configurations:

The calculations of gas transmission were performed with *Dmol*³ software package⁴ using the PBE⁵ exchange-correlation functional plus vdW correction adopting Grimme's scheme⁶ to better describe the non-bonding interaction. The lattice parameter of the cell in Figure 1 was optimized to 9.462 Å. 3D periodic boundary conditions were applied to simulate the infinitely large system; a 20 Å vacuum space in-between two sheets were set to prevent the interaction between two layers. During the calculation process, the positions of all the atoms were fully relaxed until met the following convergence criterion: 5×10⁻⁷ Ha for total energy, 1×10⁻⁴ Ha/Å for force and 1×10⁻⁴ Å for displacement. The self-consistent field computations criterion was chosen to be 10⁻⁸ Ha. The cut-off value was chosen to be 5.1 Å. The Brillouin zone for calculation was sampled by 3×3×1 k-points. The adsorption energies of each configuration were calculated by equation:

$$E_{\text{ad}} = E_{\text{graphdiyne+gas}} - (E_{\text{graphdiyne}} + E_{\text{gas}}) \quad (\text{S1})$$

where $E_{\text{graphdiyne+gas}}$ is the total energy of the graphdiyne with adsorbed gas, $E_{\text{graphdiyne}}$ is the energy of pure graphdiyne, and E_{gas} is the total energy of isolated gas molecule.

Gas transmission calculation on diffusion rate and selectivity:

The hydrogen purification behaviour by graphdiyne was quantitatively described by calculating gas diffusion rate and selectivities of H₂ to CH₄/CO using transition state theory (TST). According to TST, the rate coefficient of a reaction is given by the ratio of the flux of species through the transition state to the relative population of reactants:

$$k = \frac{k_B T}{h} \cdot \frac{Q^{TS}}{Q^{React}} \cdot e^{-E_0/k_B T} \quad (\text{S2})$$

in which Q^{TS} and Q^{React} are partition functions for the transition state (*TS*, gas in the pore center of graphdiyne) and reactant state (*React*, gas molecule at the most stable position above pores on graphdiyne), h is the plank constant, E_0 is the energy barrier value, T is the purification temperature, and k_B is the Boltzmann constant. Here to calculate the partition functions, energy levels need to be obtained first. All the translational, rotational and vibrational motions of the investigated states were treated as harmonic oscillations because their frequency could be derived by calculating the hessian matrix of the appropriate stationary states. The frequencies at these two states are summarized in Table S1.

Table S1 Adsorption energy E_{ad} and frequencies of H_2 , CH_4 and CO at React and TS.

Gas	Position	E_{ad} (eV)	Frequencies (cm^{-1}) ^a					
H_2	React	-0.07	130.08	135.13	148.49	164.29	185.10	4328.13
	TS	0.03	189.78 <i>i</i>	318.84	329.31	433.74	459.98	4310.08
CH_4	React	-0.14	70.73	72.67	90.18	204.10	238.68	297.10
			1306.27	1316.11	1324.35	1528.52	1530.82	2988.90
			3099.20	3108.04	3131.49			
	TS	0.58	148.45 <i>i</i>	210.59	218.62	304.49	319.03	402.81
CO	React	-0.11	1300.27	1318.84	1331.80	1536.03	1540.53	3043.01
	TS	0.22	3139.19	3219.92	3255.56			
			53.42	55.64	57.25	168.17	182.92	2129.10
			64.26 <i>i</i>	107.56	109.54	189.11	190.30	2089.64

^a The imaginary frequencies are denoted by *i* after values.

The next step to obtain the partition functions is to calculate the energy levels corresponding to the frequencies ν_i ($i=1-6$ for H_2 and CO , and $i=1-15$ for CH_4) in Table S1 as:

$$E_j(\nu_i)=(j+1/2)h\nu_i, (j=0, 1, 2 \dots) \tag{S3}$$

The partition functions were obtained in standard fashion as:

$$Q = \prod_{i=1}^n Q_i = \prod_{i=1}^n \frac{1}{1 - e^{-h\nu_i/k_B T}}, (n=6 \text{ for } H_2 \text{ and } CO, n=15 \text{ for } CH_4) \tag{S4}$$

with Eq.4 as defined, E_0 in Eq.2 becomes more specifically the zero-point energy difference between reactant and transition states. The diffusive selectivities of H_2 over CH_4/CO can then be derived by dividing the corresponding rate coefficients.

Large graphdiyne supercell model and corresponding gas adsorption energy

To confirm the adsorption energies and equilibrium configurations in the main text, large supercell model (a 2×2 one) as shown in Figure S1 were adopted.

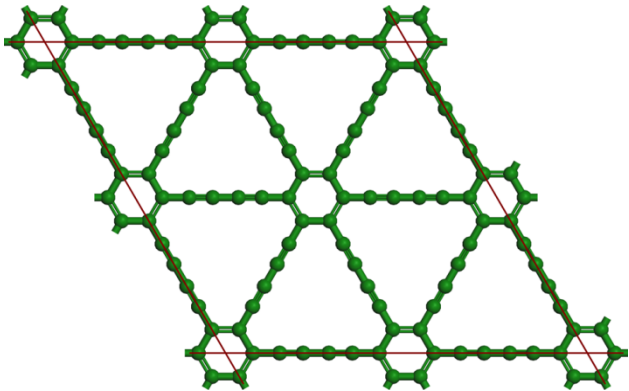


Fig. S1 Geometry structure of graphdiyne, and single cell in the large cell model calculation.

The adsorption energies and distances to the graphdiyne plane of each gas molecule at their most stable configuration are listed in the following Table S2. The values derived by small unit cell are almost the same with those listed here and are reliable.

Table S2 Adsorption energy E_{ad} and distance of H_2 , CH_4 and CO to the graphdiyne plane.

Gas	H_2	CH_4	CO
E_{ad} (eV)	-0.07	-0.13	-0.10
Distance to the graphdiyne plane (Å)	1.75	2.52	2.78

References

1 G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, 1996, **6**, 15–50; G. Kresse and J. Furthmuller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
2 P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953–17979; G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
3 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2006, **118**, 8207.
4 B. Delley, *J. Chem. Phys.* 1990, **92**, 508–517; B. Delley, *J. Chem. Phys.*, 2000, **113**, 7756–7764.
5 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
6 S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.