

Porous silicene as a hydrogen purification membrane

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We investigated theoretically the hydrogen permeability and selectivity of a porous silicene membrane via first-principles calculations. The subnanometer pores of the silicene membrane are designed as divacancy defects with octagonal and pentagonal rings (585-divacancy). The porous silicene exhibits high selectivity comparable with graphene-based membranes for hydrogen over various gas molecules (N₂, CO, CO₂, CH₄, and H₂O). The divacancy defects in silicene are chemically inert to the considered gas molecules. Our results suggest that the porous silicene membrane is expected to find great potential in gas separation and filtering applications.

Hydrogen purification from other gases is of particular importance for its energy applications partly because of the less desirable species mixed in during hydrogen production through the common methane-reforming method.¹ Taking the advantages of easy operation and low energy cost, membrane separation has been widely used in hydrogen purification.² As such, many various membranes have been developed, including metal, silica, zeolite, carbon-based and polymer membranes.^{3–7} However, since the permeability and selectivity of membranes depend sensitively on their pore size and thickness,⁸ developing high-efficiency hydrogen separation membranes with one-atom thickness and subnanometer pores is demanded.

Two-dimensional monolayer materials, such as graphene^{9–15} and h-BN,^{16–18} have attracted much research attention recently for their novel structures and properties. For example, graphene is a one-atom thick monolayer¹⁹ with unique zero-gap electronic structure and massless Dirac Fermion behavior.²⁰ Interestingly, porous graphene has been regarded as a potential ultimate membrane with one-atom thickness for hydrogen separation.^{21–28} Jiang *et al.*²¹ have demonstrated that hydrogenated and nitrogen functionalized porous graphene by removing two

neighboring rings can exhibit a high permeance for H₂ relative to CH₄. The effective size of a nanopore in a graphene membrane is the essential factor to decide its selectivity and permeability for hydrogen molecules. However, the precise control over the pore size in graphene is still a technical challenge. The other potential obstacle is the high chemical reactivity of edged carbon atoms with dangling bonds in a nanopore *versus* gas molecules, such as CO, CO₂, NO, and NO₂,^{29–31} requesting the protection of these carbon atoms with hydrogen or nitrogen atoms.²¹ Moreover, some other kinds of two-dimensional porous graphene with intrinsic subnanometer pores, such as polyphenylene,^{22,23} graphdiyne,^{25–28} and rhombic-graphyne,²⁶ have also been proposed theoretically as hydrogen purification membranes.

Very recently, silicene, a single silicon monolayer with buckled honeycomb structure,³² has received considerable interest owing to its useful chemical and physical properties,³³ including ferromagnetism,^{34,35} half-metallicity,³⁶ quantum hall effect³⁷ and giant magnetoresistance.³⁸ Experimentally, silicene can be fabricated by means of depositing silicon on Ag^{39–44} and ZrB₂⁴⁵ surfaces. Interestingly, compared with the C–C bond length in graphene (1.42 Å),²⁰ the Si–Si bond length is much longer in silicene (2.29 Å).³⁴ As a result, the divacancy defect in silicene⁴⁶ has an intrinsic pore size comparable with that of porous graphene designed by Jiang *et al.*²¹ As the divacancy defect can be easily realized in two-dimensional monolayer materials,^{47,48} it is distinctly convenient to use silicene with divacancy defects as a hydrogen separation membrane without the need to control the pore sizes.

In this work, we demonstrate that silicene with divacancy defects is an efficient hydrogen separation membrane *via* first-principles calculations. The 585 divacancy defect forms subnanometer pores in silicene. The proposed porous silicene exhibits a high permeability and selectivity of H₂ over N₂, CO, CO₂, CH₄, and H₂O. In addition, the native porous silicene is chemically inert to the considered gas molecules, implying the great advantages of silicene-based membranes over graphene-based membranes.

All the calculations are performed based on the first-principles density functional theory (DFT) implemented in the VASP

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package.⁴⁹ The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)⁵⁰ with van der Waals correction proposed by Grimme (DFT-D2)⁵¹ is chosen due to its good description of long-range vdW interactions.^{52–57} As an benchmark, our DFT-D2 calculations give a good bilayer distance of 3.25 Å and binding energy of –25 meV per carbon atom for bilayer graphene ($a = b = 2.47$ Å), which fully agree with previous experimental measurements^{58,59} and theoretical vdW calculations.⁶⁰ The climbing image nudged elastic band (CI-NEB) method⁶¹ is used for minimum energy pathway (MEP) calculations^{62,63} of the penetration of gas molecule through the porous silicene. Nine images are inserted into the initial and final states. A 6×6 supercell of silicene (72 silicon atoms) is adopted to simulate an infinite planar sheet. The energy cutoff is set to be 500 eV and the surface Brillouin zone is sampled an a 3×3 regular mesh. The vacuum space in the Z direction is about 20 Å to separate the interactions between neighboring slabs. All the geometry structures are fully relaxed until the convergence criteria of energy and force are less than 10^{-5} eV and 0.01 eV Å⁻¹, respectively. Dipole correction is employed to cancel the errors of electrostatic potential, atomic force and total energy, caused by periodic boundary condition.⁶⁴ The optimized lattice constant of silicene unit cell is 3.87 Å, agreeing with previous theoretical works.³⁴

In order to evaluate the stability of molecules adsorption on porous silicene, the adsorption energy is defined as

$$E_a = E_{\text{Gas/Silicene}} - E_{\text{Gas}} - E_{\text{Silicene}}$$

where, $E_{\text{Gas/Silicene}}$, E_{Gas} and E_{Silicene} represent the total energy of gas molecule adsorption on porous silicene, a single gas molecule, and porous silicene, respectively.

It is well known that the divacancy defect can be realized in a two-dimensional monolayer, such as graphene, using energetic particles such as electrons and ions.^{47,48} The pore in porous silicene is designed as a divacancy defect by removing two adjacent silicon atoms. As plotted in Fig. 1, the divacancy defect spontaneously forms a pair of pentagonal and one octagonal rings (585-divacancy) as happens in graphene.⁶⁵ The optimized pore size is about 4.7 Å, in good agreement with previous theoretical investigation.⁴⁶ The adsorption of various gas molecules, including H₂, H₂O, CO, CO₂, N₂, and CH₄, on the porous silicene are studied. As summarized in Table 1, the calculated equilibrium distance between molecule and silicene ranges from 2.2 to 3.1 Å. The calculated adsorption energy of H₂ on the porous silicene is about 0.06 eV and the largest adsorption energy is about 0.22 eV for H₂O considering the vdW correction. Therefore, the silicene with divacancy defects is chemically

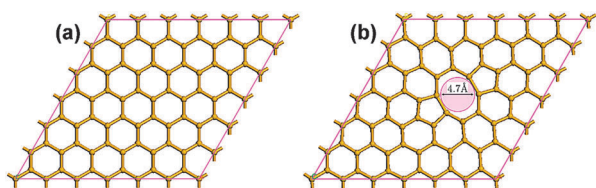


Fig. 1 Atomic geometries of (a) pure silicene and (b) porous silicene with 585-divacancy in the 6×6 supercell.

Table 1 The DFT-D2 calculated equilibrium distance D_0 (Å) between the center of gas molecules (H₂, H₂O, N₂, CO, CO₂ and CH₄) and the divacancy of silicene with corresponding binding energy E_a (eV) for gas molecules adsorption on porous silicene, and the diffusion energy barrier E_b (eV) for molecules passing through the divacancy of silicene

DFT-D2	D_0	E_a	E_b
H ₂	2.53	–0.06	0.34
H ₂ O	2.23	–0.22	0.45
N ₂	3.10	–0.07	1.03
CO	2.92	–0.18	0.99
CO ₂	3.12	–0.10	1.01
CH ₄	3.06	–0.10	1.66

inert to these gas molecules, and the gas molecules interact with porous silicene *via* weak vdW interactions.

Next, we examine the permeation of H₂ through the 585-divacancy defect of silicene. The most stable state (SS) structure of H₂ adsorption on porous silicene is that in which the axis of H₂ is parallel to the plane of silicene above the center of the divacancy, as shown in the insert of Fig. 2. To search the MEP for hydrogen permeation, we set the initial state (IS) as that in which the axis of H₂ is perpendicular to the plane with a distance of 5 Å between the center of H₂ and the divacancy of silicene.

The diffusion energy barrier is defined as

$$E_b = E_{\text{TS}} - E_{\text{SS}}$$

where, E_{TS} and E_{SS} represent the total energy of the transition state (TS) of H₂ when passing through the divacancy of silicene and the SS of H₂ adsorption on porous silicene. The MEP calculations of various gas molecules penetrating the porous silicene are plotted in Fig. 2. The diffusion energy barriers of gas molecules are summarized in Table 1. The diffusion energy barrier for H₂ through the divacancy defect of silicene is only about 0.34 eV, comparable with that of porous graphene (0.22 eV)²¹ and two-dimensional polyphenylene (0.37 eV),²³ but much smaller than that of rhombic-graphyne (0.54 eV).²⁶ This surmountable diffusion energy barrier of H₂ suggests that a hydrogen molecule can permeate the porous silicene at

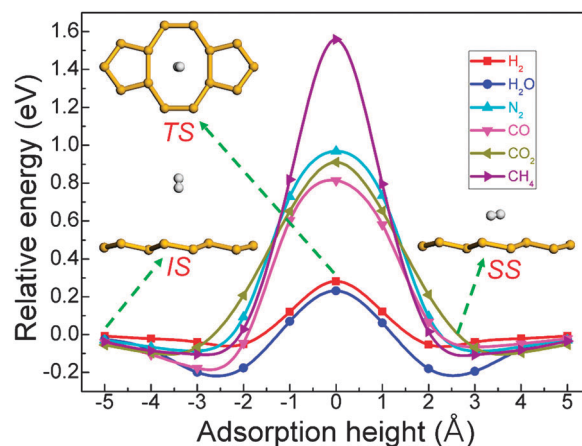


Fig. 2 Energy profiles for H₂, H₂O, N₂, CO, CO₂ and CH₄ passing through the divacancy of silicene as a function of adsorption height.

moderate temperature and pressure. The optimized structures of the TS show that H₂ passes the divacancy defect with the H–H bond axis perpendicular to the silicene surface.

The calculated diffusion energy barriers are 1.03, 0.99, 1.01 and 1.66 eV for N₂, CO, CO₂ and CH₄, respectively, which are much larger than that of H₂ (0.34 eV). Thus, porous silicene with divacancy defect can block these gas molecules and works as an ideal hydrogen purification membrane. For an H₂O molecule, the calculated diffusion energy barrier is about 0.45 eV, which is slightly larger than that of an H₂ molecule. Thus, an H₂O molecule can permeate the porous silicene as an H₂ molecule does and porous silicene may be used as a new water purification membrane.^{66–68}

To examine the hydrogen separation efficiency of porous silicene, the selectivity for H₂ relative to other gas molecules (H₂O, N₂, CO, CO₂ and CH₄) through the divacancy defect of silicene is estimated with the Arrhenius equation^{21,22,26}

$$S_{\text{H}_2/\text{Gas}} = \frac{r_{\text{H}_2}}{r_{\text{Gas}}} = \frac{A_{\text{H}_2} \exp\{-E_{\text{H}_2}/k_{\text{B}}T\}}{A_{\text{Gas}} \exp\{-E_{\text{Gas}}/k_{\text{B}}T\}},$$

where r is the diffusion rate, A is the diffusion prefactor, and E is the diffusion energy barrier. Assuming that the diffusion prefactors of these gas molecules are identical ($A = 10^{11} \text{ s}^{-1}$),²³ the temperature-dependence diffusion rate and selectivity profiles are calculated, as shown in Fig. 3. The diffusion rates of H₂ molecules are much higher than those of N₂, CO, CO₂, and CH₄, but little higher than that of an H₂O molecule, consistent with the calculated diffusion energy barriers. Meanwhile, the selectivity of H₂ over N₂, CO, CO₂, and CH₄ is extremely high for a wide temperature range. At room temperature ($T = 300 \text{ K}$), we find a high selectivity on the order of about 10^{11} , 10^{11} , 10^{11} and 10^{22} for H₂ over N₂, CO, CO₂ and CH₄, respectively (Table 2). Compared with traditional silica (H₂/N₂ and H₂/CO₂ range from 10 to 10^3)^{3,4} and graphene-based membranes (H₂/CH₄ ranges from 10^8 to 10^{23}),²¹ the porous silicene exhibits high selectivity for H₂ over various gas molecules, including N₂, CO, CO₂, and CH₄. Note the calculated H₂ selectivity of porous silicene is an ideal theoretical result.

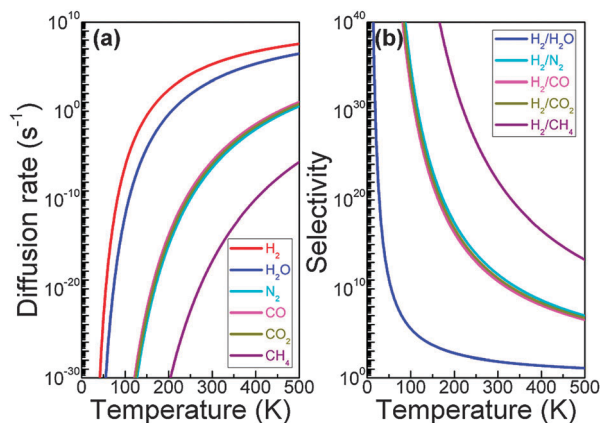


Fig. 3 (a) Diffusion rate and (b) selectivity for gas molecules (H₂, H₂O, N₂, CO, CO₂ and CH₄) passing through the divacancy defect of silicene as a function of temperature.

Table 2 The DFT-D2 calculated selectivity (S) of H₂ relative to other gas molecules at room temperature ($T = 300 \text{ K}$), including H₂/H₂O, H₂/N₂, H₂/CO, H₂/CO₂ and H₂/CH₄, and corresponding comparison results (diffusion energy barrier E_{b} (eV) for H₂ and selectivity S for H₂ relative to other gas molecules) of previously proposed porous membranes

Membranes	Silicene	Graphene	Silica
Reference	This work	Ref. 21	Ref. 3
$E_{\text{b}}(\text{H}_2)$	0.34	0.22 ^a , 0.33 ^b	—
$S(\text{H}_2/\text{H}_2\text{O})$	10^2	—	—
$S(\text{H}_2/\text{N}_2)$	10^{11}	—	10^2
$S(\text{H}_2/\text{CO})$	10^{11}	—	—
$S(\text{H}_2/\text{CO}_2)$	10^{11}	—	10
$S(\text{H}_2/\text{CH}_4)$	10^{22}	10^{23} , 10^8	10^3

^a Hydrogenated porous graphene in ref. 21. ^b Nitrogen functionalized porous graphene in ref. 21.

The permeability and selectivity for traditional hydrogen separation membranes largely depend on many other factors in practical applications, including crystalline defect and membrane thickness.

The calculated selectivity of H₂ over H₂O molecules is distinctly smaller. However, the selectivity value of 10^2 for H₂ over H₂O at room temperature is still superior for effective separation.²⁵ In addition, gas water can be removed from H₂/H₂O mixed gas simply by reducing their temperature due to its higher freezing point compared with H₂.

Finally, we explain why the porous silicene with divacancy defect is chemically inert to gas molecules, such as H₂, H₂O, N₂, CO, CO₂, and CH₄. In the porous graphene proposed by Jiang *et al.*,²¹ the edged carbon atoms in the pore have distinct dangling bonds, as shown in Fig. 4(a). The carbon atoms with dangling bonds possess high chemical reactivity *versus* gas molecules,^{29–31} which request the protection of edged carbon atoms with hydrogen or other functional groups. Removing two adjacent silicon atoms from silicene also generates dangling bonds on edged silicon atoms, as shown in Fig. 4(b). However, the neighboring silicon atoms form covalent Si–Si bonds spontaneously, resulting in the self-saturation of their dangling bonds, as shown in Fig. 4(c). Thus, the porous silicene with divacancy defect is native chemically inert to the considered gas molecules. Our test calculations on the graphene with divacancy defect confirm this interpretation. The porous graphene with divacancy defect is also chemically inert to most considered gas molecules due to the self-saturation of dangling bonds on edged carbon atoms by forming C–C covalent bonds, but then the pore size is too small for hydrogen separation.⁶⁹

In summary, we have demonstrated that silicene with divacancy defect can be used as an ideal hydrogen separation membrane using first-principles density function theory. H₂ can permeate the porous silicene with a surmountable diffusion energy barrier of 0.34 eV. The porous silicene exhibits a high selectivity on the order of 10^2 , 10^{11} , 10^{11} , 10^{11} and 10^{22} for H₂ over H₂O, N₂, CO, CO₂, and CH₄ at room temperature, respectively. Compared with graphene-based membranes, the divacancy defect in silicene can be easily experimentally realized without need to control the pore size. Moreover, the porous silicene is chemically inert to most gas molecules. Taking these advantages, our studies imply the great potential

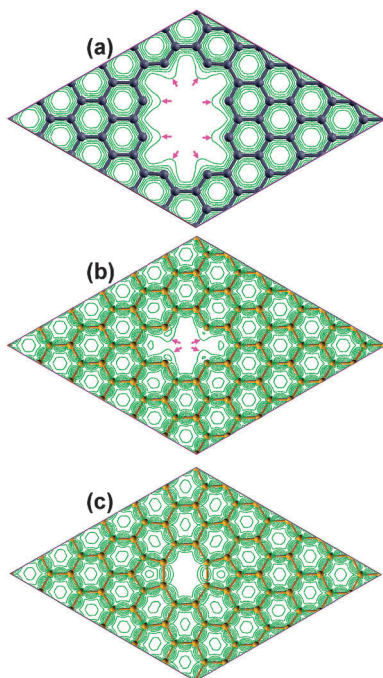


Fig. 4 Differential charge density of (a) porous graphene without hydrogen saturation proposed by Jiang *et al.*²¹ and porous silicene with (b) unrelaxed and (c) relaxed divacancy defect in the 6×6 supercell. The isosurfaces are projected on the surfaces and marked by green lines. The dangling bonds are marked by pink arrows.

of porous silicene in hydrogen separation applications. It should be mentioned, however, that silicene can be obtained on the substrate of Ag or ZrB_2 , and it is still a challenge to get a free-standing silicene monolayer.

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