

Helium separation *via* porous silicene based ultimate membrane

Cite this: *Nanoscale*, 2013, 5, 9062

Wei Hu,^a Xiaojun Wu,^{ab} Zhenyu Li^a and Jinlong Yang^{*a}

Helium purification has become more important for increasing demands in scientific and industrial applications. In this work, we demonstrated that the porous silicene can be used as an effective ultimate membrane for helium purification on the basis of first-principles calculations. Pristine silicene monolayer is impermeable to helium gas with a high penetration energy barrier (1.66 eV). However, porous silicene with either Stone–Wales (SW) or divacancy (555 777 or 585) defect presents a surmountable barrier for helium (0.33 to 0.78 eV) but formidable for Ne, Ar, and other gas molecules. In particular, the porous silicene with divacancy defects shows high selectivity for He/Ne and He/Ar, superior to graphene, polyphenylene, and traditional membranes.

Received 7th May 2013

Accepted 3rd July 2013

DOI: 10.1039/c3nr02326e

www.rsc.org/nanoscale

Introduction

Helium, the lightest noble gas, has wide applications in fundamental research, medical, and industrial fields with an inexorably increasing consumption at present.^{1,2} However, helium storage on earth is limited and the natural production of helium on earth, mostly by α -decay of radioactive metals in the mantle, is far too slow. As the helium is inert, only a few natural gas fields have helium concentration high enough for economical separation using physical methods, such as cryogenic distillation or pressure-swing adsorption.³ Taking advantage of easy operation and low energy cost, membranes have been widely used in helium separation.⁴ Various membranes have been developed, such as polymer and silica membranes, and their permeability and selectivity largely depend on the pore size and membrane's thickness.^{5–7} For this purpose, developing a highly efficient helium separation membrane with atomic thickness and sub-nanometer pores is highly desirable.

In recent years, two-dimensional monolayer materials have attracted much research attention for their novel properties and wide potential applications in electronics and energy storage *etc.* In particular, graphene, a single atomic layer of graphite,^{8–12} has been regarded as an ultimate membrane with atomic thickness¹³ for gas separation, including hydrogen^{14–21} and helium^{22–28} purification. Since pristine graphene is impermeable for helium,^{22,23} porous graphene is needed with controlled pore size at sub-nanometer for effective helium separation.^{26–28} Leenaerts *et al.*²³ have investigated the defective graphene and found that the experimentally observed vacancy defects, such as Stone–Wales

(SW) and divacancy (555 777 or 585) defects,^{29–31} still present a high penetration energy barrier for helium. Removing more neighboring carbon atoms from graphene may produce suitable sub-nanometer pores in graphene for helium separation, but the precise control of pore sizes in graphene is still a technical challenge.¹⁴ Another potential obstacle is the high chemical reactivity of edged carbon atoms with dangling bonds in porous graphene,^{32–34} requesting the protection of these carbon atoms with hydrogen or nitrogen atoms.¹⁴ To overcome these obstacles, some porous graphenes with intrinsic subnanometer pores, such as polyphenylene,³⁵ have also been proposed theoretically for hydrogen^{15,16} and helium^{24,25} separation.

Recently, silicene, a single silicon monolayer with buckled honeycomb structure,³⁶ has been successfully fabricated experimentally on metallic and ceramic substrates, including Ag,^{37–42} Ir⁴³ and ZrB₂.⁴⁴ Semiconducting substrates for silicene have also been proposed theoretically *via* first-principles calculations, such as h-BN,⁴⁵ SiC,⁴⁶ Si, diamond⁴⁷ and ZnS,⁴⁸ for new silicene-based nanoelectronic devices. Much research effort has been devoted to investigate its notable physical properties,⁴⁹ such as ferromagnetism,^{50,51} half-metallicity,^{52,53} quantum hall effect,⁵⁴ giant magnetoresistance⁵⁵ and superconductivity.⁵⁶ Adsorption of different atoms on silicene has been also studied theoretically.^{57–60} Silicene has a longer Si–Si bond (2.29 Å)⁴⁶ than the C–C bond (1.42 Å)¹² in graphene. Thus, the common defects in silicene, such as divacancy defects, may have intrinsic pore size comparable with that of porous graphene by removing more neighboring carbon atoms.¹⁴ Moreover, our previous theoretical work⁶¹ has shown that the 585 divacancy defect in silicene is chemically inert to most of gas molecules and porous silicene can block big molecules, such as N₂, CO, CO₂ and CH₄. It provides a possibility to fabricate porous silicene with some common defects for helium separation.

^aHefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China. E-mail: jlyang@ustc.edu.cn

^bCAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China

In this paper, we demonstrated that porous silicene with intrinsic vacancy defect is a good candidate for helium separation on the basis of density functional theory calculations with van der Waals correction. Especially, we considered the penetration behaviors of noble gas molecules, including He, Ne and Ar. We showed that the porous silicene with SW, 555 777, or 585 defect presents a surmountable barrier for helium (0.33 to 0.78 eV) but formidable for Ne, Ar and other gas molecules. In particular, the porous silicene with divacancy defect shows high selectivity for He/Ne and He/Ar, superior to graphene, polyphenylene, and traditional membranes.

Theoretical models and methods

The optimized lattice parameter of silicene is 3.87 Å, in good agreement with previous theoretical works.⁵⁰ In order to simulate the infinite planar monolayer, a 6×6 supercell of silicene containing 72 silicon atoms is adopted. Both perfect and defective porous silicene monolayers are studied, including the SW, 555 777 or 585 defect, as plotted in Fig. 1. The vacuum space in the z direction is about 20 Å to separate neighboring slabs.

All calculations are performed based on the first-principles density functional theory (DFT) implemented in the VASP package.⁶² The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)⁶³ with van der Waals correction proposed by Grimme (DFT-D2)⁶⁴ is chosen due to its good description of long-range vdW interactions.^{65–72} As a benchmark, our DFT-D2 calculations give a good bilayer distance of 3.25 Å and a binding energy of –25 meV per carbon atom for bilayer graphene ($a = b = 2.47$ Å), which fully agree with previous experimental measurements^{73,74} and theoretical vdW calculations.^{75,76} The climbing image nudged elastic band (CI-NEB) method⁷⁷ is used for minimum energy pathway (MEP) calculations^{78,79} of the penetration of gas molecule through the porous silicene. Nine images are inserted between the initial and final states. The energy cutoff is set to be 500 eV and the surface Brillouin zone is sampled with a 2×2 regular mesh. All 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.⁸⁰

Previously, we have shown that porous silicene is chemically inert to most gas molecules existed in natural gas, such as N₂, CO, CO₂ and CH₄.⁶⁰ In order to evaluate the stability of porous silicene in noble gas environment, we calculated the adsorption energy of noble gas molecules 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 energies of noble gas adsorption on silicene, noble gas, and silicene, respectively.

Results and discussion

We first examine the adsorption behaviors of noble gases (He, Ne and Ar) on perfect and defective silicene. The structure of the most stable state (SS) is that the noble gas molecule adsorbs on the center of the pore in silicene with the distance ranging from 2.98 to 3.52 Å. The calculated adsorption energy show that they are all physically adsorbed on silicene *via* weak vdW interactions, as summarized in Table 1. Thus, the porous silicene is chemically inert to noble gases without additional hydrogen and nitrogen atoms to protect the edged silicon atoms in defects, showing great advantages over previously prospered graphene used for gas separation.¹⁴

Next, we investigate the MEP of noble gas molecule penetration through both the perfect and porous silicene with various defects. The physisorbed structure is set as the initial state's (IS's) structure, and the configuration of the physisorption on the opposite side is set as the final state (FS). For instance, the calculated MEPs for noble gas molecules passing through the porous silicene with either 555 777 or 585 defect are shown in Fig. 2. The energy barrier is defined as $E_b = E_{\text{TS}} - E_{\text{SS}}$, where the E_{TS} and E_{SS} represent the total energy of the transition state (TS)

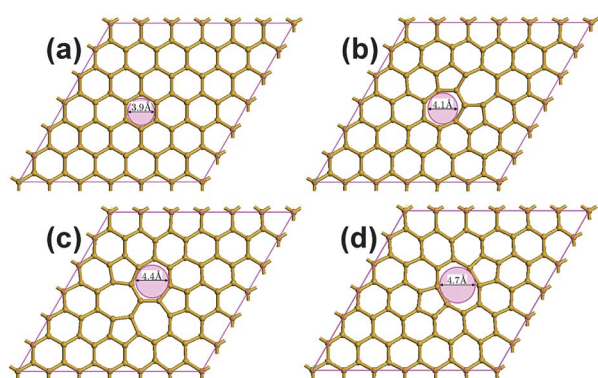


Fig. 1 The optimized structures of (a) pristine silicene and porous silicene with (b) the SW defect, (c) 555 777 and (d) 585 divacancy, respectively. Note that the 555 777 divacancy is more stable than the 585 one with a small energy gain of –0.67 eV similar to graphene.³¹

Table 1 Calculated equilibrium distance D_0 (Å) between the center of noble gases (He, Ne and Ar) and the pore of silicene with corresponding adsorption energy E_a (meV) for noble gases on perfect and defective silicene with DFT-D2 method

DFT-D2	D_0	E_a
He/perfect	3.33	–15.9
Ne/perfect	3.20	–42.5
Ar/perfect	3.52	–62.4
He/SW	3.09	–16.8
Ne/SW	3.00	–45.5
Ar/SW	3.26	–66.7
He/555 777	3.01	–14.1
Ne/555 777	3.00	–43.9
Ar/555 777	3.15	–58.0
He/585	3.01	–13.9
Ne/585	2.98	–42.1
Ar/585	3.01	–67.9

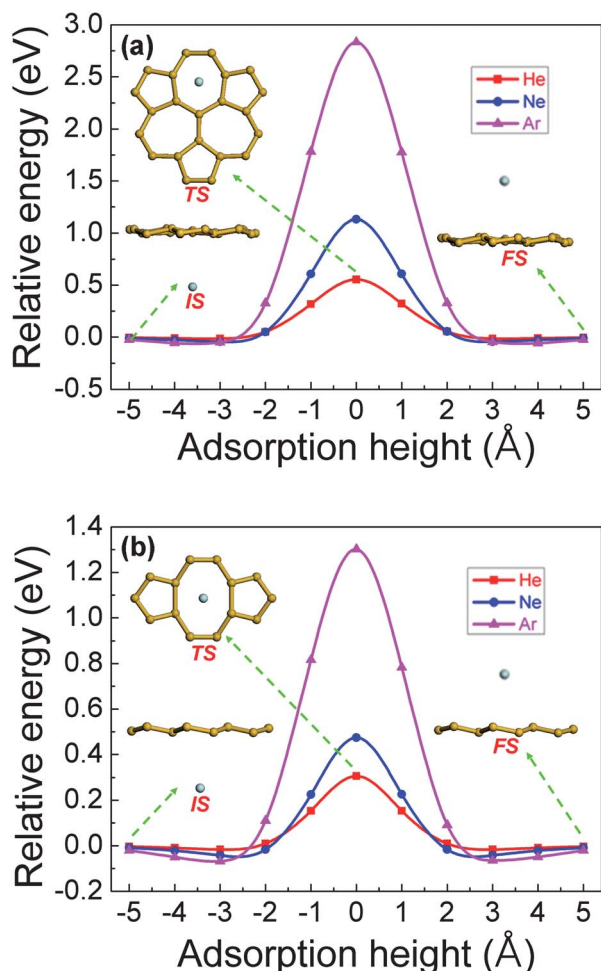


Fig. 2 Energy profiles for He, Ne, and Ar passing through the divacancy defects ((a) 555 777 and (b) 585) of silicene as a function of adsorption height.

of He passing through the pore of silicene and the SS of He adsorption on silicene, respectively.

The calculated penetration energy barriers of noble gases (He, Ne and Ar) passing through both the perfect and defective silicene, as well as those through graphene,²³ are summarized in Table 2. The perfect silicene presents large penetration energy barriers of about 1.66, 3.58, and 7.27 eV for He, Ne and Ar, respectively. Although these values are largely smaller than that of He passing through the perfect graphene (11.69 eV),²³ the perfect silicene is still impermeable to the noble gas molecules. However, the SW, 555 777, and 585 defects create sub-nanometer pore in silicene with the size of 4.1, 4.4, and 4.7 Å,

Table 2 Calculated energy barrier E_b (eV) for the penetration of noble gases (He, Ne and Ar) passing through silicene and graphene with DFT-D2 method

Membrane	Silicene	Graphene ²³
Noble gas	He, Ne, Ar	He
Perfect	1.66, 3.58, 7.27	11.69
SW	0.78, 1.55, 3.48	6.12
555 777	0.57, 1.18, 2.89	5.75
585	0.33, 0.53, 1.41	3.35

respectively, which largely reduces the penetration energy barrier for noble gas molecules. For example, the penetration energy barriers of helium molecule passing the porous silicene with SW and 555 777 defects are about 0.78 and 0.57 eV, respectively, which are significantly smaller than that through the perfect silicene. Note that the threshold energy barrier for gas penetration is about 0.5 eV.²⁴

In particular, the porous silicene with 585 divacancy defect presents a surmountable penetration energy barrier of about 0.33 eV, which is comparable with that of partial nitrogen functionalized porous graphene (0.21 eV)²⁶ and polyphenylene (0.43 eV),¹⁵ but smaller than that of all hydrogenated porous graphene (0.64 eV).²⁶ Thus, helium molecule can penetrate the porous silicene with 585 divacancy defects at moderate temperature and pressure. However, the penetration energy barriers for Ne and Ar are 0.53 and 1.41 eV, respectively, suggesting that the porous silicene with 585 divacancy defect is still impermeable for Ne and Ar molecules. Moreover, our recent theoretical work²⁵ has shown that porous silicene with 585 divacancy defect is impermeable to most of common gas molecules (N_2 , CO, CO_2 and CH_4). Thus, the porous silicene can be used as a very promising monolayer for helium purification.

To examine the helium separation efficiency of porous silicene, the selectivity for He relative to other noble gases (Ne and Ar) through the divacancy defects of silicene is estimated with the Arrhenius equation¹⁴

$$S_{He/gas} = \frac{r_{He}}{r_{gas}} = \frac{A_{He} \exp\{E_{He}/RT\}}{A_{gas} \exp\{E_{gas}/RT\}}$$

where r is the diffusion rate, A is the diffusion prefactor, and E is the diffusion barrier. Assuming that the diffusion prefactors of noble gases are identical ($A = 10^{11} \text{ s}^{-1}$),¹⁵ T -dependence diffusion rates and selectivities are calculated and shown in Fig. 3. As summarized in Table 3, the porous silicene exhibits higher permeability and selectivity for noble gas separation at room temperature, as compared to porous graphene, such as polyphenylene,¹⁵ which has a low selectivity of about 6×10^2 for He/Ne.

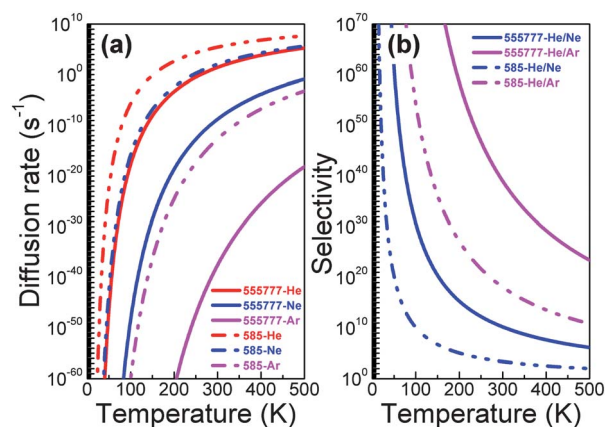


Fig. 3 (a) Diffusion rate and (b) selectivity for noble gases (He, Ne and Ar) passing through the divacancy of silicene as a function of temperature. Solid and dotted lines represent porous silicene with the 555 777 and 585 divacancy defects, respectively.

Table 3 Calculated selectivity (S) of He relative to other noble gases (He/Ne and He/Ar) passing through porous silicene at room temperature ($T = 300$ K), and corresponding comparison results on energy barrier E_b (eV) and selectivity S of previously proposed porous membranes

Membrane Reference	Silicene This work	Graphene Ref. 26	Polyphenylene Ref. 15
E_b (He)	0.33, ^a 0.57 ^b	0.64, ^c 0.21 ^d	0.43
S (He/Ne)	2×10^3 , 2×10^{10}	—	6×10^2
S (He/Ar)	1×10^{18} , 2×10^{39}	—	1×10^{30}

^a Porous silicene with the 555 777 divacancy defect in this work. ^b Porous silicene with the 585 divacancy defect in this work. ^c All hydrogenated porous graphene in ref. 26. ^d Partial nitrogen functionalized porous graphene in ref. 26.

Finally, we revealed the origin of high selectivity for He relative to other noble gases (He/Ne and He/Ar) when passing through the divacancy defects in silicene. The effective pore widths¹⁴ of 555 777 and 585 divacancy defects in silicene are about 2.1 and 2.3 Å, respectively, which are slightly smaller than the kinetic diameter of He (2.6 Å).¹⁵ Thus, helium atom passes through the divacancy defects by overcoming a small diffusion energy barriers. However, the kinetic diameters of Ne (3.2 Å) and Ar (3.4 Å) are much larger than the effective pore widths of the divacancy defects in silicene, which make them pass through the divacancy with high energy barriers.

Conclusions

In summary, we have demonstrated that porous silicene can be used for noble gas separation with high permeability and selectivity on the basis of first-principles calculations. He gas can pass through the 555 777 and 585 divacancy defects of silicene easily with low energy barriers of 0.57 and 0.33 eV, and exhibiting high selectivity for He/Ne and He/Ar. Compared with graphene-based membranes, the divacancy defects in silicene can be easily experimentally realized without the need to control the pore sizes and additional protection of edged atoms in defects. To be mentioned, it is still a challenge to get free-standing silicene monolayer currently. However, from the viewpoint of technology, the porous silicene deposited on a porous substrate can still be used for filtering applications, as the porous substrate supported porous graphene.¹⁵

Acknowledgements

This work is partially supported by National Key Basic Research Program (2011CB921404, 2012CB922001), by NSFC (21121003, 91021004, 20933006, 11004180), by Strategic Priority Research Program of CAS (XDB01020300), and by USTCSCC, SC-CAS, Tianjin, and Shanghai Supercomputer Centers.

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