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Versatile two-dimensional stanene-based membrane for hydrogen purification

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ABSTRACT

The two-dimensional (2D) honeycomb graphene lattices were demonstrated to be promising hydrogen separation membranes. To effectively operate as hydrogen separation membranes, porous defects and enlargement of pores in these materials must be created. The defect-free 2D stanene (Sn), which is realized in experiment, possesses densely packed intrinsic pores as large as 4.66 Å. This work analysed honeycomb 2D Sn-based membranes for hydrogen purification using density functional theory calculations, and found that a fluorinated 2D Sn membrane exhibits excellent hydrogen purification. This purification performance was then tuned for better balanced permeability and selectivity by applying a moderate strain to the membrane. The defect-free fluorinated 2D Sn membrane was identified as suitable for hydrogen purification.

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Introduction

Hydrogen is regarded as an environmental-friendly energy carrier due to its high energy density per weight, and the fact that there are no greenhouse gas emissions released during its utilization [1–5]. Currently, hydrogen is produced via steam reforming from natural gas in industry, which is the most common and economical process at a large scale [1]. The byproduct of the steam reforming consists primarily of CO and CH₄ [6]. In order to obtain pure hydrogen for industrial applications like fuel cell, a hydrogen purification process is required to remove CO and other impurities [7,8]. 2D membranes including g-C₃N₃ [9], graphdiyne [10,11], polyphenylene [12], and Fused Pentagon [13] have been systematically investigated and demonstrated to remove the impurities due to their high efficiency and low energy consumption compared to traditional separation methods [14–19].

An ideal 2D membrane for hydrogen purification would show a good balance of separation selectivity and permeability [20,21]. Generally, high gas permeability increases the diffusion rate of production gas, while high selectivity results in a high purity production gas [22]. Current 2D membranes are limited by a near universal trade-off between permeability and selectivity for hydrogen purification where a membrane with high throughput (permeability) has low selectivity, and vice versa [21]. Robeson quantified this relationship between permeability and selectivity by an empirical upper bound relationship expressed by the log of the selectivity factor and

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2D honeycomb lattice membranes including graphene, silicene and germanene have also been used to purify hydrogen. The tiny pore sizes of pristine graphene and silicene have been proven to be impermeable to H_2 , and defects, which enlarge the pore size, have to be introduced in order to promote their permeability [23,24]. 2D stanene, a new family member of 2D honeycomb lattice has been fabricated successfully by molecular beam epitaxy [25]. Theoretical calculations predicted that the pore size of 2D Sn is significantly larger pore size than graphene, silicene and germanene, and can be further enlarged by decorating with F [26,27], which could make it a promising membrane for H_2 separation. In addition, strain is another method to enlarge the pore size. The application of strain to these membranes provides a practical strategy to tune the permeability.

In this work, we demonstrate that 2D Sn-based membranes with densely packed uniform pores, could be effective for H_2 purification. The 2D Sn-based materials can be further engineered by a moderate strain to achieve the best desired H_2 permeability. In addition, The H_2 purification performances of 2D Sn-based membranes were compared with previously studied 2D membranes based on a theoretical upper bound model constructed in this work. 2D SnF is highlighted to be an effective new material for H_2 purification when taking both permeability and selectivity into account.

Computational method

Density functional theory calculations

Density functional theory (DFT) calculations were conducted by using the Vienna Ab-initio Simulation Package (VASP) [28,29]. The exchange-correlation interactions were treated within the generalized gradient approximation (GGA) [30] with the Perdew-Burke-Ernzerhof (PBE) functional [31]. The van der Waals interaction was described by the empirical correction in Grimme's scheme, i.e. DFT + D3 [32]. The electron wavefunctions were expanded by plane waves with cut-off energies of 500 eV, and the convergence criteria for residual force and energy on each atom during structure relaxation were set to 0.005 eV/Å and 10^{-5} eV, respectively. The vacuum space was more than 20 Å, which was enough to avoid the interaction between periodical images. The climbing image nudged elastic band (NEB) was used for finding saddle points and minimum energy paths. The 2 \times 2 \times 1 supercell membranes with a K-point of $6 \times 6 \times 1$ grid in reciprocal space were used during geometry optimization and NEB calculations. The phonon frequencies [33] of 2D two membranes were obtained by phonon calculations to confirm the dynamical stabilities of membranes.

Diffusion and selectivity calculations

The diffusion barrier was calculated by Eq. (1):

 $E_{\text{b}}=E_{\text{TS}}-E_{\text{IS}}$

(1)

Where, the E_{TS} and E_{IS} are the total energy (eV) of the transitional state (TS) and the initial state (IS, the optimized states of gases adsorbed on membranes), respectively.

The diffusion rate (k, s^{-1}) was estimated based on the diffusion barrier (E_b) using the Arrhenius equation as done in pervious works [23]:

$$\mathbf{k} = \mathbf{A} e^{\left(-\frac{E_{\mathbf{b}}}{k_{\mathbf{b}}T}\right)} \tag{2}$$

Here, the diffusion perfector A is an empirical relationship between temperature and diffusion rate, was set to an identical ($A = 10^{11} \text{ s}^{-1}$) as suggested by Stephan Blankenburg et al. [34]. K_b and T are the Boltzmann constant and absolute temperature, respectively. The rate of selectivity was calculated by dividing the diffusion rate of H₂ ($k(H_2)$) by that of another gas, like CO₂, as shown the following equation.

$$S_{H_{2/gas}} = \frac{k(H_2)}{k(gas)} = e^{\left(\frac{E_b(gas) - E_b(H_2)}{k_B T}\right)}$$
(3)

To take the pore density (ρ , m⁻²) into account, the H₂ permeability (P(H₂), s⁻¹ m⁻²) was obtained by Eq. (3):

$$P(H_2) = \rho^* k(H_2) \tag{4}$$

Where, the pore density (ρ) is the number of pores per square meter (m²) of the membrane.

Results and discussions

Structure and characteristics

The stanene (2D Sn) and fluorostanene (2D SnF) models are constructed based on experimental results [25]. The DFT optimized structures of 2D Sn and SnF were shown in Fig. 1a-d. In contrast to the planar geometry of graphene, a low-buckled configuration was found to be more stable for the 2D Sn and SnF with the honeycomb pores distributed on the surfaces uniformly and naturally, because this enhances the overlap of π and σ orbitals [26]. The equilibrium lattice constant for 2D Sn is 4.66 Å, which is much larger than that of graphene (2.46 Å) [35] and of silicene (3.87 Å) [36]. The lattice constant can be further enlarged to 4.97 Å by fluorination. The pore sizes of honeycomb lattice materials are equal to their lattice constants. With the intrinsic honeycomb pores, 2D Sn-based membranes possess the largest pore densities (5.32 \times 10 18 m $^{-2}$ for 2D Sn, and 4.67 \times 10 18 m $^{-2}$ for 2D SnF) among previous investigated H₂ purification membranes, for instance $g-C_3N_3$ (2.28 \times 10¹⁸ m⁻²) [9]. High density of pores reduces the membrane area required to separate a given amount of gases mixture and is a parameter beyond the traditional trade-off relation which enables membranes to obtain high permeability without reducing the selectivity. In addition, the fluorination of stanene results in sp³ hybridized fluorostanene (2D SnF, Fig. 1b,d) that has enhanced chemical inertness toward the adsorption of syngas, similar to the effect that occurs in fluorinated graphene [37,38]. Therefore, these 2D Sn-based membranes can be expected to serve as superior membranes compared to traditional porous materials.

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Sn SnF Sn SnF **(b) (e) (f) (g)** (a) 6 20 Sn SnF 18 5 16 10 14 4 12 Stress (N/m) Frequency (THz) Frequency (THz) 3 10 8 2 (d) (c) 6 4 2 0 0 0.0 0.2 0 1 Strain

Fig. 1 – The structures of Sn and SnF from top (upper) and side (lower) views (a-d). (e-f) the phonon dispersion spectrum of Sn and SnF. (g) the stress strain curves of Sn and SnF.

The stabilities of Sn and SnF membranes were examined by phonon calculations as shown in Fig. 1e-f. No imaginary frequency is found in the phonon dispersion spectrum of both 2D Sn and SnF, indicating that both membranes are dynamically stable. To include the effect of strain, biaxial strains were subjected on the systems by varying the lattice parameters, a and b. The strain-stress relationships of 2D Sn and SnF were then determined directly under a biaxial strain that ranged from 0% to 20%, as shown in Fig. 1g. The absence of an abrupt energy variation in Fig. 1g indicates that both 2D Sn and SnF could sustain large strain deformation up to 20% without any structural destruction. Due to the buckled honeycomb structures of stanene and fluorostanene, the strain enlarges the pore size with a small value of elongation in the Sn-Sn bond length. For instance, a 5% strain applied to the two membranes enlarges the pore size by 5%, while Sn-Sn bond lengths in Sn and SnF are only increased by 3.7% and 4.4% respectively. Therefore, a large pore size is obtained by strain without significantly affecting the stability of membranes.

Permeability of syngas through the 2D Sn

To examine the permeability of syngas (H₂, CO, and CH₄) through the 2D Sn and SnF, the diffusion barriers were calculated by NEB method. The minimum energy pathways for these gases passing through the 2D Sn under 0%, 5%, 8% and 10% strains are plotted in Fig. 2. Under strain free conditions, the diffusion of (large) CH₄ through 2D Sn induces a structural destruction of 2D Sn, so the diffusion barrier is therefore not shown in Fig. 2a. For the other two gases, the diffusion barrier for H₂, and CO is 0.92 eV and 2.33 eV, respectively. With such a large diffusion barrier, pristine 2D Sn is impermeable to these gases at room temperature. One feasible and economic solution to conferring permeability in 2D Sn is the application of strain, since a small strain could increase the membrane's pore size. As the membrane was

subjected to strain, the diffusion barriers for H_2 , CO and CH₄ decreased significantly. For example, the diffusion barriers reduced to 2.96, 1.68 and 0.61 eV for CH₄, CO and H₂, respectively under a strain of 5% (Fig. 2b), which further reduced to 2.38, 1.32 and 0.48 eV at a strain of 8% (Fig. 2c). Under 10% strain, the diffusion barrier of H₂ decreased to 0.40 eV (Fig. 2d) which is lower than the threshold value for gas diffusion (about 0.50 eV) [39], while the diffusion barrier of other two gases remained above the threshold barrier (0.5 eV). Thus, a moderate strain can be expected to enhance H₂ purification of 2D Sn performance by increasing its permeability.

Permeability of syngas through the 2D SnF

For 2D SnF, the larger lattice constants (about 6.7% larger than that of 2D Sn) could make 2D SnF a better candidate for H₂ purification. The minimum energy pathways of various gases passing through the 2D SnF under different strains are plotted in Fig. 3. Without strain, the diffusion barriers for H₂, CO, and CH₄ through the 2D SnF are 0.66, 2.04 and 2.92 eV, respectively (Fig. 3 a). All these values are smaller than that of 2D Sn. Even so, the 2D SnF is still difficult for H₂ to permeate since the diffusion barrier is larger than the threshold value (0.5 eV), except under high temperature or high pressure. Like pure stanene, the permeability of H₂ through 2D SnF is also tunable by a small strain deformation. Under 5% strain, the diffusion barriers for H₂, CO, and CH₄ through the 2D SnF are 0.42, 1.3 and 2.08 eV (Fig. 3b), which can be further reduced to 0.26, 0.81 and 1.30 eV (Fig. 3d), respectively, under a strain of 10%. Among the range of the strain deformation, only the diffusion barrier of H₂ is reduced to much smaller than the threshold value (0.5 eV) for gas diffusion while the diffusion barriers for other gases are still larger than 0.5 eV, which indicates that 2D SnF should be highly selective and only permeable to H₂. Thus, the 2D SnF is a potential membrane for H_2 purification.

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Fig. 2 – The minimum energy pathways for H_2 , CO, and CH_4 passing through the 2D Sn in the presence of 0%, 5%, 8% and 10% strains.



Fig. 3 – The minimum energy pathways for H_2 , CO, and CH_4 passing through the 2D SnF in the presence of 0%, 5%, 8% and 10% strains.

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Fig. 4 – Diffusion rate (a) and selectivity (b) of gases (H_2 , CO and CH_4) diffusion throng 2D Sn and SnF under different strains (0% and 10%).

H₂ purification performance on 2D Sn and SnF

To quantitatively examine the H₂ purification performance on 2D Sn and SnF membrane materials, gas diffusion rates and selectivities of H₂ from CO/CH₄ were calculated based on the Arrhenius equation (see Eqs. (2) and (3)) and plotted as functions of temperature as shown in Fig. 4a and b, respectively. Without strain, the H₂ diffusion rates through 2D Sn, and SnF are 3.0×10^{-5} s⁻¹, 8.2×10^{-1} s⁻¹ at room temperature respectively, which indicates these membranes are both

impermeable for H₂ diffusion at room temperature. Meanwhile the selectivities of H₂/CO separation are 8.5 \times 10²³, 2.8 \times 10²³, respectively at room temperature, which are extremely high. Since the diffusion barriers can be effectively reduced under strain deformation as demonstrated above, the diffusion rate will significantly increase based on Eq. (2), but at the price of selectivity due to its dependence on the diffusion barrier difference between gases. Under 10% strain, the gas diffusion rates on 2D Sn and SnF increased markedly to 1.6 \times 10⁴ s⁻¹, 4.0 \times 10⁶ s⁻¹ respectively, while the selectivity of



Fig. 5 – (a) The relationship of diffusion barriers and pore sizes, (b) The Upper bound correlation for H₂/CO purification. The value of graphdiyne, polyphenylene, g-C₃N₃ and Fused Pentagon is collected from references 21, 23, 20 and 24 and calculated by Eq. (4), respectively.

Please cite this article in press as: Gao G, et al., Versatile two-dimensional stanene-based membrane for hydrogen purification, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016 https://freepaper.met///write//dx.doi.org/10.1016 H₂/CO reduced little, to 1.1 \times 10¹², 2.3 \times 10⁹, respectively at room temperature. Clearly, better balance and performance can be achieved under a moderate strain for H₂ purification.

The effects of the strain on the diffusion barrier of various gases in the syngas through 2D Sn and SnF were examined by investigating the relationship between diffusion barriers and pore-sizes (Fig. 5a). In both of the membranes, the diffusion barriers of CO and CH₄, which are relatively large molecules, have steep negative linear relationships with the pore size. While, the diffusion barriers of H₂, which are relatively small, reduce gradually with the pore size. Therefore, the diffusion barriers towards CO and CH₄ are more sensitive than H₂ to the pore sizes. Increasing pore size by strain would reduce the selectivity of H₂/CO and H₂/CH₄. In addition, the fitted line of the diffusion barriers of these gases through 2D SnF is higher than the corresponding fitted line for that of 2D Sn. If the pore sizes of these two membranes are the same, gas can pass through 2D Sn with a lower diffusion barrier than that of 2D SnF due to a steric effect caused by fluorine-decoration.

Finally, the H₂ purification performances of 2D Sn and SnF were compared by taking both permeability and selectivity into account. The upper bound correlation for H₂/CO based on our calculated and references' results is plotted in Fig. 5b. The H₂ permeability increases with the strain in both membranes, while the H₂/CO selectivity decreases. A dashed line was fitted to all data points in Fig. 5b as the upper bound line. The membrane with best H₂ purification performance are located in the upper right corner of Fig. 5b. The results of 2D SnF at different strains, and polyphenylene [12] are located at the upper right of the upper bound line (Fig. 5b), while the results of Sn, graphdiyne [10], $g-C_3N_3$ [9] and fused pentagon [13] are located at the lower left of the upper bound line. It is worth noting that, even though the H₂ permeability of graphdiyne, g- C_3N_3 and fused pentagon are very high, the selectivity in each case is relatively low, which locates them below the upper bound line. Therefore, 2D SnF is an excellent membrane for H₂ purification when taking both permeability and selectivity into account.

Conclusions

The H_2 purification performances of pristine and F-decorated 2D Sn membranes under different strains were systematically investigated by DFT calculations. Two strategies, strain and fluorination, increased the pore size and enhanced the permeability of 2D Sn. Combing fluorination with proper strain enabled us to achieve superior H_2 purification performances compared to other traditional porous materials. Our calculations highlight a new interesting material for H_2 separation for further experimental validation.

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