Computational Materials Science 143 (2018) 277–285

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

The mechanisms study of the porous graphene for the purification of the mixed gases: A multi-scale computational method

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ARTICLE INFO

Article history:
Received 9 June 2017
Received in revised form 6 November 2017
Accepted 8 November 2017

Keywords:
Porous membrane
Density functional theory
Molecular dynamic
Gas separation

ABSTRACT

Molecular dynamic (MD) simulations, grand canonical Monte Carlo (GCMC) simulations, and density functional theory (DFT) were used to study the ability of four different graphene slices with H-deactivated pores (HP6, HP10, HP13, and HP16) for the separation of H_2 from the mixed gases. It was found that the HP10, with its proper pore size of 2.96 Å, can effectively separate H_2 from CO. The HP13 can effectively separate H_2 from CO_2 and CH_4 with its high H_2 selectivity of 5.8×10^{10} and 6.4×10^{24}, respectively. Different from the other studies on the permeation of gas only induced by size sieving, the porous graphene can exhibit high H_2 selectivity and permeability over other gases. It was further revealed that the adsorption energy, barrier energy, size sieving, gas distribution, and gas motion also play a role in blocking the transmission of the mixed gas through the porous graphene.

1. Introduction

It is well known that the H_2 purification is in great demand in the industrial production and scientific research. Generally, the common method of steam-methane re-forming [1] to produce H_2 usually generates some other gases, such as CO_2, CO, and CH_4. Thus, it is necessary to purify H_2 from these gases because of its special usage [2]. Different from conventional methods of gas purification, membrane purification of gases is more promising because of its critical advantages: lower energy costs, smaller works, and simple operation [3]. Actually, many kinds of membranes have been studied, such as metal, zeolite, and polymer membranes [4–7]. However, those membranes often show poor tolerance to high temperatures and corrosive solvents. Recently, graphene has been proven to be an excellent material for developing size-selective molecular separation membranes due to its critical advantages: atomic thickness, good mechanical strength, and remarkable chemical stability [8,9]. On the other hand, it was found that the ideal graphene does not allow gases to diffuse because the strong electron density of six-membered rings prohibits particles from passing through the six-membered rings [10,11]. Subsequently, the porous graphene is used to realize gas molecule separation. Here, the pores in graphene slices can be made by many methods [12–14] and the pores formed can make gas permeate at different diffusion rates. As a result, it was shown that the porous graphene can be used to effectively separate gases with good permeability [15–20]. Moreover, the gas purification ability of the porous graphene slices can be handled by changing the sizes, the pore's shape, and the chemical processing of graphene. Although theoretical studies based on the first-principles computations have been widely performed to explore the applications of the porous graphene for gas purification [15–22]. However, the thermodynamics and kinetics analyses of gas phase transport through the isolated porous graphene have been rarely reported to the best of our knowledge.

In this study, the different porous graphenes have been employed to separate H_2 from mixed gases. In the porous graphene, the loss of several carbon atoms in the membrane can induce dangling bonds of high chemical activity [21]. Generally, hydrogen atom is used to stabilize vacancies in graphene. As a result, the electroneutrality of the porous graphene will also be changed upon introduction of hydrogen atoms. So, some questions arise, i.e., how does this affect the graphene's purification of H_2 from the mixed gases? Moreover, how do the size of nanopore and the interaction of mixed gases influence the graphene's separation of H_2 from the mixed gases? To answer these questions, a systematic study is carried out in this study to address the performance of H-deactivated porous graphene membranes for the separation of H_2 from mixed gases employing the DFT, GCMC, and MD

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https://doi.org/10.1016/j.commatsci.2017.11.016
0927-0256/

simulation. Firstly, the barrier energy for the H_2, CO, CO_2, and CH_4 passing through the pore of graphene is calculated using DFT. After then, the adsorption energy for these gas molecules on the porous graphene membrane has been obtained by GCMC simulations. Moreover, to explore the permeation ability of the mixed gases, MD simulations are performed for H_2/CO, H_2/CO_2, and H_2/CH_4 passing through the different-sized pores of graphene.

2. Models and methods

As shown in Fig. 1, the pores are made by removing some atoms from the center of the graphene slices. In this study, four different-sized pores have been considered, which are named as HP6, HP10, HP13, and HP16, respectively. To avoid the displacement of the entire graphene slice, the position of the graphene slice has been fixed except for the hydrogen atom.

Before MD simulation, the DMol^3 module has been employed to optimize the structure of the graphene slice using DFT [23]. 6×6 supercells are built to simulate original planar slices. A vacuum region of 20 Å is set along the z direction to avoid interactions among the periodic images. Then, the H-deactivated porous graphene membranes are fully optimized. The Perdew–Burke–Ernzer hof (PBE) exchange correlation potential and the double numerical basis set containing polarization functions (DNP) are employed during the calculations [21,24,25]. To optimize the structure of the graphene slices, we choose 5×10^{-3} Å for displacement, 2×10^{-5} Ha for total energy, 10^{-6} Ha for the self-consistent field (SCF) computation criterion, and 4×10^{-3} Ha/Å for force, respectively. To increase the speed of SCF convergence, the direct inversion of the iterative subspace technique with a subspace size of 6 is applied on this module [21,25]. According to the dispersion-corrected method, the synchronous approach with the conjugated gradient refinements is used to search transition states (TS). The energy difference between the TS and the most stable adsorbing states (SS) is used to calculate the diffusion energy barriers (E_b) for gas passing through the pore.

Moreover, a combination of Sorption module and GCMC simulations is applied to confirm the intermolecular interactions between graphene and gas molecules. GCMC simulations [26] of gas molecules adsorption are based on the COMPASS force field. The intermolecular interactions are evaluated by an Ewald sum of electrostatic interactions with an accuracy of 10^{-5} kcal/mol. The van der Waals interactions are calculated using atom-based approach with 15.5 Å cutoff length, 0.5 Å buffer width, and 1.0 Å spline width. The ration of the exchange, conformer, rotation (including the maximum amplitude of 5°), translation (including the maximum step of 1 Å) and regrowth step type used in the simulation are conducted randomly as 39%, 20%, 20%, 20%, and 2%, respectively. Six million Monte Carlo steps are set to simulate each point on the isotherm, in which the first three million steps are set to equilibrate the system correctly and the remaining steps are set to gain the production.

To explore the gas diffusion behavior of the graphene membranes, MD simulations in the NVT-ensemble are conducted, where the force field of the condensed-phase optimized molecular potential (COMPASS) is selected to run atomistic simulation studies. COMPASS has been proven to be suitable for the determination of many material properties in previous studies [27,28]. According to the modeling method reported previously [10], as shown in Fig. 2, two layers of graphene membranes are used to build the simulation box, where 80 H_2 and 80 CO, CO_2 or CH_4 molecules are placed in the regions between two layers, respectively. A 30 Å vacuum region is set in both sides of the box, which is defined as permeation regions. The size of the model is about 30 Å × 30 Å × 80 Å with periodic boundary conditions. In the process of simulation, the hydrogen atoms on the edge of the pores are allowed to move, while the carbon atoms in graphene are fixed. The Andersen thermostat is used to maintain a constant temperature (298 K). The particle motion is conducted by a velocity Verlet algorithm with a time step of 1 fs. The electrostatic interactions are evaluated by the Ewald method. The trajectories are recorded every 5 fs. Note that the simulation method mentioned above has been successfully adopted previously [10,29,30].

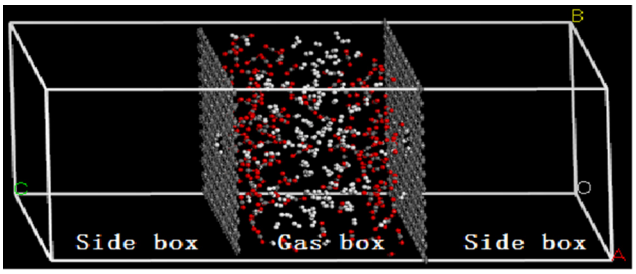

Fig. 2. Schematic of the simulation box with two porous graphene slices and mixed gas in MD simulation. (C, gray; O, red; and H, white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

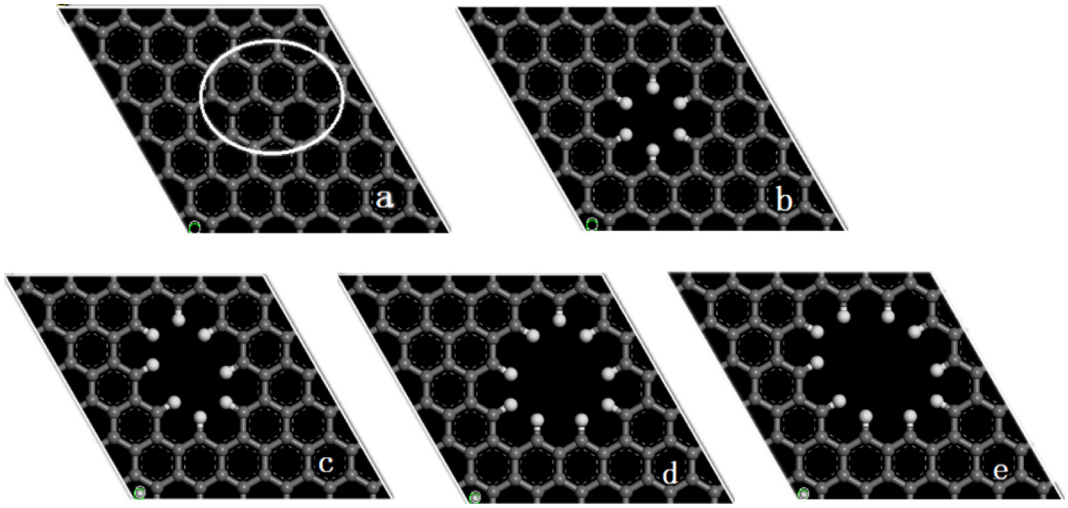

Fig. 1. Sketch of the models for the graphene slices used in this study. (a) original graphene slice, (b) HP6, (c) HP10, (d) HP13, (e) HP16. Color code: C, gray; H, white.