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Graphene with line defect as a membrane for gas separation: Design via a first-principles modeling

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ABSTRACT

A new line defect consisting of a sequence of octagons and all-hydrogen passivated pores in graphene was designed as a gas separation membrane using first-principles calculations. The all-hydrogen passivated pore produces a formidable barrier of 1.5 eV for CH_4 but an easily surmountable barrier of 0.12 eV for H_2. Hence it exhibits extremely high separation capability in favor of H_2 among all studied species with the selectivity on the order of 10^{22} for H_2/CH_4. These results suggest that such a line-defect-containing graphene-based membrane could play a great role on numerous clean energy applications.

1. Introduction

Gas separation such as hydrogen purification is of great importance for the study of new clean energy techniques [1], and a lot of materials have been developed for this purpose [2,3]. Compared to traditional systems, the membrane system as an efficient filter for gas mixtures without any phase change obviously reduces the energy cost [4]. Therefore, development of novel and energy efficient membranes for gas separation is currently attracting immense research interest.

Even though various polymeric membranes exhibit good selectivity towards different gas molecules [5–7], challenges of developing polymeric membranes with high permeability and long-lived gas separation performance were already encountered. Carbon molecular sieve [8,9], as one of the porous inorganic membranes, has been developed with great efforts to provide better selectivity and thermal and chemical stability. However, carbon molecular sieve is intrinsically brittle and fragile, hence careful preparation is required [10].

The isolation of a free-standing sheet of graphene in 2004 opened a whole new branch in material science [11], leading to new insights in physics, chemistry and applied science. Its mechanical strength, chemical inertness and 2D monolayer structure make it a suitable candidate as a separation membrane. Actually, since the permeability of a membrane is inversely proportional to its thickness [12], the permeability of graphene-based membrane can be enhanced tremendously because of the one-atom thickness of a graphene. Understanding the transportation of atoms and molecules through such a truly 2D membrane is not only for fundamental interest but also for its usefulness in a number of applications such as proton exchange membranes in fuel cells, separating gases to increase the sensitivity of chemical sensors, and separation of CO_2 from exhaust gas combinations.

Unfortunately, the pristine graphene is impermeable to gases as small as helium [13]. This is due to the fact that the electron density of its aromatic rings is substantial enough to repel atoms and molecules trying to pass through the hollows. Therefore, to achieve gas permeability, it is necessary to destroy its aromatic structures. Recently, researcher sculpted closely spaced nanopores within suspended graphene using a focused electron beam of the transmission electron microscope [14]. In addition, porous 2D sheets have been created by assembling molecular building blocks [15]. Improvements in these techniques may be helpful for creating ordered subnanometer-sized pores within graphene which may then be used as a 2D molecular-sieve membrane.

Previously, porous graphene as a gas separation membrane has been investigated theoretically using quantum mechanical and molecular dynamics simulations. Sint et al. studied the diffusion rates of solvated ions passing through functionalized graphene nanopores driven by an external electric field [16]. De-en Jiang et al. used a porous graphene with nitrogen functionalization to separate H_2 and CH_4 [17]. S. Blankenburg et al. demonstrated that the presented porous graphene exhibits an extremely high selectivity in favor of H_2 and He among other atmospheric gases [18]. Moreover, H. Du et al. presented a porous graphene with various pore shapes for separation of H_2 and N_2 [19]. These studies highlighted that the porous graphene

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exhibits selectivity either towards ions and gas molecules. Recently, one-dimensional extended line defects in graphene have been observed experimentally, which stemmed from structural mismatch during the growth of graphene on a metal surface [20–23]. In general, the embedded line defects divide the graphene into domains with different orientations and thus can affect the electronic, thermal, and mechanical properties of graphene [24,25]. The controlled formation of extended 1D defect in graphene opens up an exciting possibility for graphene-nanodevices. Among those line defects, a line defect [21], containing octagonal and pentagonal sp^2-hybridized carbon rings, may hold great potential for the application of graphene as a membrane material for gas separation, which has not been investigated up to now.

In this paper, we computationally explored the electronic properties and separation capabilities of line-defect-containing graphene (LD-G) as well as LD-G with missing octagons passivated by hydrogen (H-LD-G) via first principles calculations. The selectivity of the two porous graphene-based membranes for different gas species (He, H_2, N_2, O_2, CO, CO_2 and CH_4) was also calculated. It is expected that the results presented in this paper may help to intensify the potential applications of graphene in the field of gas separation.

2. Methodology

All calculations were carried out using the Vienna ab initio simulation package (VASP) with generalized gradient approximation (GGA) and the projector-augmented wave (PAW) method [26–28]. A cutoff energy of 400 eV was used for plane wave expansion of electron wave function. The graphene with line defect in a supercell contains 84 C atoms, and a vacuum region of 15 Å normal to graphene plane was set in order to minimize surface interactions. The Brillouin zone was sampled by a $5\times5\times1$ k-point mesh within the Monkhorst–Pack scheme [29]. All structures were fully relaxed until the force acting on each atom was smaller than 0.02 eV/Å. To determine the diffusion barrier between the given initial and final states, the climbing image nudged elastic band (CI-NEB) method was adopted [30,31]. Five intermediate images between initial and final states were constructed by interpolation as starting guesses for NEB calculations. All images were linked to each other by elastic springs and optimized along the reaction path with regard to the force convergence criteria of 0.05 eV/Å.

3. Results and discussion

Fig. 1a depicts the optimized structure of the LD-G in which a line defect is composed of repeated pentagon pairs and octagons. Given that the bond lengths labeled in Fig. 1a are slightly changed, the less strained domains induced by such a structural defect are observed, which is in line with the fact that all C atoms are almost in the same plane. Such a line defect basically keeps the sp^2 hybridization of the carbon atoms of graphene intact. The calculated total density of states (TDOS) shown in Fig. 1b indicates that the line defect presents metallic properties because of the existence of a spike around the Fermi level. Due to the reduced symmetry in this line defect, the projected density of states (PDOS) of five carbon atoms (C1–C5) which are labeled in Fig. 1a are analyzed in order to find the contribution to the metallic characteristics. As shown in Fig. 1b, it is found that the main contributions to the states around the Fermi level originate from the 2p orbitals of carbon atoms (C1–C4) which belong to the line defect, while the C5 atom which is far away from the defect exhibits no contribution. All these structural and electronic properties are in good agreement with Lahiri's results [21].

Considering that the size of the octagon within the line defect structure is larger than that of aromatic ring in pristine graphene, the strength of π system around the octagons has been weakened. Therefore, the octagon may extend the applications of graphene as a membrane material for selective diffusion of atoms or molecules. To explore the separation capability of the octagonal ring, He and H_2 were chosen as target molecules due to the small size of the molecules, and

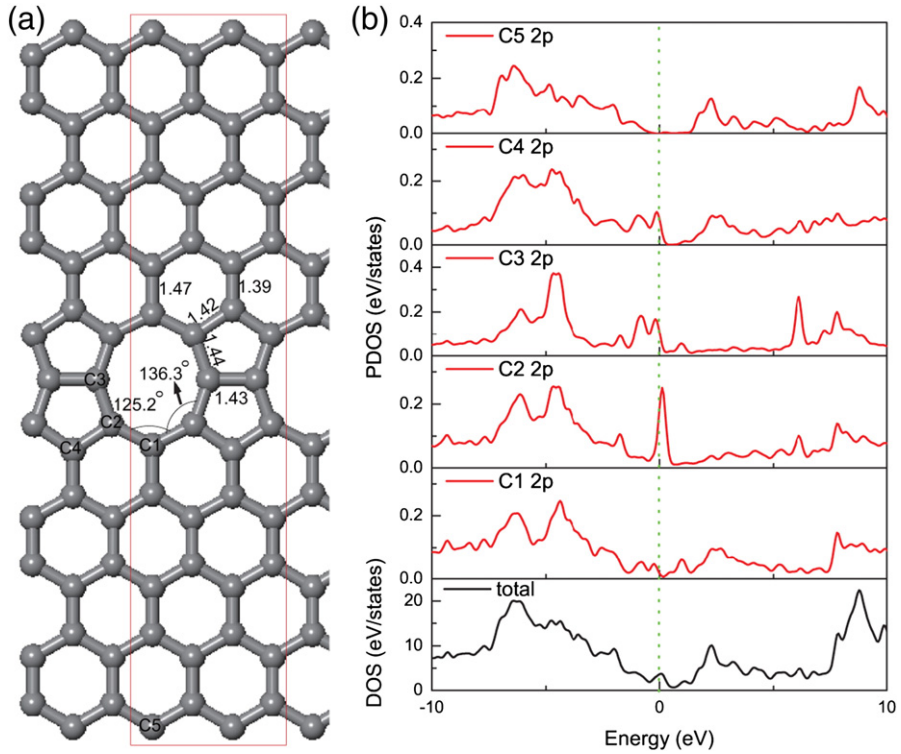

Fig. 1. (a) Optimized configuration of LD-G. The red rectangle indicates a unit cell. (b) The total DOS of the LD-G and the PDOS of the C atoms in the LD-G. The Fermi level is set to zero.