INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 5037–5042

Available online at www.sciencedirect.com

ScienceDirect

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

Computational prediction of experimentally possible g-C_3N_3 monolayer as hydrogen purification membrane

*Zhinan Ma, Xudong Zhao, Qing Tang, Zhen Zhou**

Tianjin Key Laboratory of Metal and Molecule Based Material Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Computational Centre for Molecular Science, Institute of New Energy Material Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, PR China

ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form
8 January 2014
Accepted 10 January 2014
Available online 10 February 2014

Keywords:
g-C_3N_3 layer
Hydrogen purification
Gas separation membrane
Density functional theory

ABSTRACT

Membrane technology has been used for hydrogen purification. In this work, two-dimensional g-C_3N_3 monolayer was proposed as an effective hydrogen separation membrane on basis of density functional theory computations. The structure of g-C_3N_3 monolayer was optimized first, and the computed phonon dispersion confirmed its stability and supported the experimental feasibility. The permeability of H_2 and impurity gases, including CO, N_2 and CH_4, was investigated. Compared with H_2, it is more difficult for the impurity gases to penetrate through g-C_3N_3 monolayer. The high selectivity of H_2 vs. CO, N_2, and CH_4 ensures a superior capability to conventional carbon and silica membranes. With high H_2 permeability and selectivity, g-C_3N_3 monolayer is a potential H_2 purification membrane.

1. Introduction

In response to energy crisis, hydrogen energy has aroused much interest in the whole world for its environment-friendly nature. With the development in economy, science and technology, large-scale hydrogen production is probable on a longer timescale [1]. In application, H_2 purification is an important stage for its utilization and storage [2]. Therefore, finding an effective and low-cost strategy for H_2 purification is a challenge in hydrogen economy. Though varied methods have been applied nowadays, membrane separation is considered the outstanding one because of convenient operation, energy saving, and compatibility with the environment [3]. Various membranes for H_2 separation can be classified as three types: polymeric, inorganic (such as metal, silica, ceramic, carbon, and zeolite), and hybrid [4–15]. To achieve high H_2 permeation and selectivity in a membrane, thin thickness is a critical condition because of its inverse proportion to permeation [16]. Consequently developing an ultrathin membrane with high performance is highly expected for H_2 separation.

Since graphene was realized experimentally, two-dimensional (2D) materials with particular chemical and

* *Corresponding author*. Tel.: +86 22 23503623; fax: +86 22 23498941.
E-mail address: zhouzhen@nankai.edu.cn (Z. Zhou).

0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2014.01.046

physical properties attract huge attention and provide new ideas for H_2 separation membranes because of the ultrathin thickness up to one atom [17–19]. Graphene has been considered a candidate as H_2 purification membrane for a time. However, perfect graphene is not capable of permeating gases, due to the compact atom arrangement [20]. Therefore, porous graphene was expected as a superior separation membrane [21,22]. For example, Jiang et al. proposed that graphene could acquire high selectivity for H_2 vs. CH_4 by removing two neighboring carbon rings [19]. In another work, a series of pores were introduced to graphene for separating H_2 from H_2/N_2 mixing gases, and the results demonstrated that the selectivity and permeability could be controlled by shapes and sizes [23]. Very recently, few-layered graphene and graphene oxide membranes with nanopores have been explored for selective gas transport and hydrogen separation in experiments [24,25]. These membranes with structural defects showed improved hydrogen selectivity, which is in good agreement with previous computational reports [19,23,26–29]. Similar to graphene, computations disclosed that designed defects could also increase the gas permeability of silicene for hydrogen purification [30]. Though porous graphene has high H_2 selectivity, controlling graphene with particular pore sizes and homogeneous distribution is a large challenge. Therefore, membranes with intrinsic pores are highly desired for H_2 purification. An experimentally available 2D polyphenylene is prospective. Li et al. proved it to possess high selectivity for H_2 permeation [31]. With B or N doping and tensile stress, 2D polyphenylene exhibited tunable H_2 permeability [32–34]. Graphdiyne, an $sp–sp^2$ hybridized 2D carbon material, was also suggested as an excellent separation membrane especially for H_2/CH_4 separation [35–37].

As mentioned above, it is extremely difficult to achieve large-area porous graphene. Also, the active dangling bonds of the carbon atoms along pores, easily poisoned by some unexpected gases, obstruct the application of graphene. Recently, graphitic carbon nitride layer (g-C_3N_3) has been explored in experiments [38,39], and the electronic properties of infinite 2D g-C_3N_3 layer were investigated computationally [40]. In experiments a carbon nitride sample ($CN_{0.96}$) was prepared, and was considered a form of graphite-like carbon nitride (g-CN) [38], which was denoted as g-C_3N_3 to distinguish from g-C_4N_3 [40]. In experiments, g-C_3N_3 was found to self assemble in nanotube bundles, nanoribbons and microspheres [39]. Is graphene-like g-C_3N_3 monolayer experimentally possible? With intrinsic pores and no dangling bonds, could g-C_3N_3 monolayer be used as hydrogen purification membrane? To address the above questions, in this work, by density functional theory (DFT) computations, we investigated the structure and stability of g-C_3N_3 monolayer. We also studied the penetration of H_2, CO, N_2 and CH_4 through g-C_3N_3 2D monolayer and explored the selectivity and permeability of g-C_3N_3 for H_2.

2. Computation details

Our DFT computations were performed through an all-electron method implemented in DMol^3 code [41]. The generalized gradient approximation (GGA) for exchange-correlation term was employed. Double numerical basis sets with polarized function (DNP) and PBE functional were adopted for g-C_3N_3 structure optimization and band structure computations [42]. To describe gas adsorption on g-C_3N_3 layer and gas penetration through g-C_3N_3 layer, we introduced van der Waals (vdW) correction with Grimme's scheme (DFT-D2), which is a semiempirical method for long-range dispersion correction [43]. The global orbital cutoff was set 6.5 Å. The self-consistent field (SCF) procedure was used with a convergence threshold of 10^{-6} au on the total energy. All the Brillouin-zone integrations of the computations were performed on 6 × 6 × 1 k-points. The transition states were searched by synchronous method with conjugated gradient (CG) refinements [44]. This method performs linear synchronous transit (LST) maximization firstly and several quadratic synchronous transit (QST) maximizations subsequently. LST maximization and each QST maximization stage are followed by CG minimizations for locating a transition state. A 1 × 1 cell was employed for the geometry optimization of g-C_3N_3 monolayer. Gas separation was studied within a 2 × 2 supercell. All the computations were performed with a vacuum space lager than 10 Å in the Z direction.

The phonon dispersion spectrum of g-C_3N_3 was computed by CASTEP code by employing GGA in the PBE exchange-correlation functional [42,45]. The cutoff energy was chosen as 480 eV, and other details were consistent with the above computations.

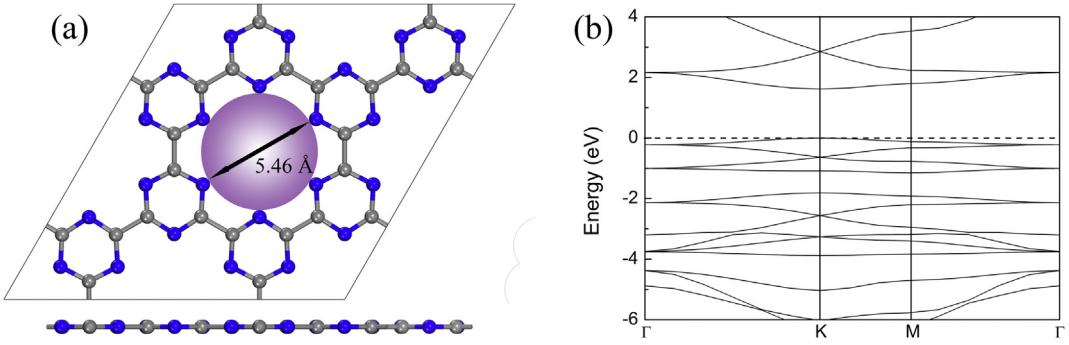

Fig. 1 – (a) Top and side view of g-C_3N_3 monolayer in a 2 × 2 supercell with 5.46 Å diameter pore. (b) Band structure for g-C_3N_3 monolayer.