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Two-dimensional graphene-like C_2N: an experimentally available porous membrane for hydrogen purification

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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We theoretically demonstrate that two-dimensional porous C_2N sheet exhibits an extremely high selectivity and large permeance in favour of H_2 among other atmospheric gases. This experimentally available porous C_2N is superior to traditional membranes, such as polymers and silica, and could have great potential for hydrogen separation.

Due to the depletion of fossil fuel and increased environmental problems, a great deal of attention has been focused the search for clean and renewable energy. Hydrogen has been identified as an attractive alternative energy source because of its efficiency, natural abundance, and environmental friendliness.[1] Hydrogen can be produced through steam reforming of methane by partial oxidation of methane[2] which contains undesirable gas molecules including CO_2 and CO[3]. Thus, separating H_2 from these species through a cost-effective and efficient way is of particular importance for its storage and usage[3]. Membrane technology[4,5] is considered to be most promising approach, among the various strategies for H_2 separation, due to the advantages of easy operation, high energy efficiency, and low cost. Many kinds of membranes have been developed for this target and applied in industries, such as metallic[6], silica[7], zeolite[8] and polymer[9] membranes. Graphene based porous membranes with one-atom thickness has been attracted particular interest in the research of H_2 separation, because the permeance of a membrane is inversely proportional to its thickness[10-14]. Jiang *et al.*[10] first reported that the porous graphene by removing two neighboring rings from a graphene sheet can present a formidable barrier (1.6 eV) for CH_4 but easily surmountable for H_2 (0.22 eV) in theory, which suggests that porous graphene are far superior to traditional membranes. However, the realization of this kind of pore in graphene is rather challenging in experiment, even without the cost issue. Therefore, several graphene like membranes with intrinsic and synthetically defined porous structures have been proposed for the purpose of H_2 separation[12-16]. Li *et al.*[13] investigated the capability of two-dimensional polyphenylene for separating H_2 from other gas molecules, such as CO, CO_2, and CH_4, which shows remarkably high selectivity for H_2 separation. Graphdiyne with suitable pore size was proved as a superior membrane for H_2 purification over CH_4, but not for CO_2 and CO[14]. Zhang *et al.*[15] reported that the H_2 permeability and selectivity over other gas molecules is mostly governed by the pore sizes. The experimental results have demonstrated that the porous graphene oxide membrane is very good for gas selectivity[17, 18]. Thus, the exploration of atomic-thick structures with more appropriate pore size for H_2 purification is needed.

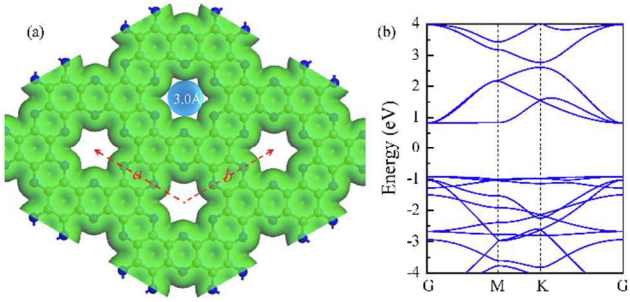

Figure 1 (a) Top view of 2D porous C_2N sheet in a 2 × 2 supercell. The dashed lines indicate the two vectors of the unit cell. Pore electron density isosurface of 2D porous C_2N sheet is also displayed (isovalue of 0.05 e/Å^3). Carbon and Nitrogen atoms are denoted with gray and blue balls, respectively. (b) Electronic band structure of 2D porous C_2N sheet.

Recently, a new micrometre-sized two-dimensional (2D) N-containing holey crystals: C_2N, was synthesized via a simple wet-logical reaction as a bottom-up approach without template assistance[19]. There are hexagonal pores naturally and uniformly distributed with the same shape in 2D C_2N. The width of pore is estimated to be 3.0 Å as shown Fig. 1, which is larger than the kinetic diameter of H_2 (2.89 Å)[20], but smaller than those of CO_2, and CO (3.30, and 3.76 Å)[21]. This implies that 2D porous C_2N may sever as two-dimensional molecular-sieve membranes for gas separation. One-atom thickness of 2D porous C_2N sheet is another exciting feature for acting as an ultimate membrane. In this work, we performed density functional theory (DFT) computations to demonstrate the hydrogen purification capability of the 2D porous C_2N sheet with naturally and uniformly distributed pores.

All the calculations were performed by using the VASP package[22-24]. The generalized-gradient approximation (GGA) with Perdew-Burke-Erzenhoff (PBE)[25] exchange–correlation functional was employed for the spin-unrestricted calculations. Van der Waals (vdW)[26,27] interaction was employed to evaluate the strength of the interactions between molecules such as H_2 and CO with 2D porous C_2N sheet. In the preliminary search and optimization, the equilibrium adsorption configurations for molecular gases were fully relaxed without any symmetric constraints. The relative diffusion barrier calculations have been performed by using the climbing-image nudged elastic band method (CI-NEB)[28]. The convergence tolerance of the energy was set to 10^{-5} eV, and the maximum allowed force were 0.01 eV/Å. A vacuum region of 20 Å was applied in the z direction to ensure negligible interaction between adjacent layers. First principles molecular dynamics (FPMD) were applied to simulate the events of molecules passing-though the pores of 2D porous C_2N sheet. Constant-temperature simulations with a time step of 1 ps at 300 K were performed.

Fig. 1a presents the optimized structure of 2D porous C_2N sheet, which is composed of two benzene rings are bridged by pyrazine rings, which consist of a six-membered D2h ring with two nitrogen atoms facing each other. The optimized lattice parameter for 2D porous C_2N sheet is a = b = 8.354 Å (which is also the distance between two pores), and agrees well with the experimental value (8.3 Å)[18]. Two different types of carbon bonds are present in benzene rings: 1.428 and 1.467 Å (out and in pyrazine rings). The C-N bond length is 1.336 Å. The angle of C-N-C is 117.4º, slightly deviated from 120 º. Fig. 1b illustrates the band structure of 2D C_2N sheet and indicates that 2D C_2N is a semiconductor with band gap of 1.74 eV. It is in good agreement with previous theoretical results (1.70 eV), but smaller (by approximately 0.22eV) than the experimental results (1.96 eV)[19] determined by optical absorbance method. The underestimation of the Kohn–Sham treatment of the DFT is well known. Both the valence band maximum (VBM) and conduction band minimum (CBM) are located at the gamma point. There are unusual flat bands near the CBM and VBM, because the π-electronic structure in the benzene ring is isolated by pyrazine rings. It is different with other graphene or graphene like 2D semiconductors, which makes the 2D C_2N unique.

Moreover, we plotted the electron-density isosurface of 2D porous C_2N sheet a rather low value of 0.05 e/Å^3 in Fig. 1a. The pore width in 2D porous C_2N is about 3.0 Å. The pore size is in-between kinetic diameters of H_2 and other molecular, such as CO and CO_2, indicating the possible application in hydrogen purification. Before calculating the diffusion barrier, we examined several configurations for H_2, CO and CO_2 molecules adsorption on top of the pore, respectively. The most stable configurations are that the axis of molecule are perpendicular to the surface of 2D porous C_2N sheet. The adsorption energy is -0.05 eV for H_2 with a height of 1.8 Å. For CO_2 and CO, the adsorption energy are -0.12 and -0.15 eV, respectively. These indicate weak vdW interaction between molecules and 2D porous C_2N sheet.

To investigate the capability of 2D porous C_2N sheet for separating H_2 from several gas molecules, including CO, and CO_2, diffusion barriers of these molecules passing though 2D porous C_2N sheet have to be calculated. We applied the CI-NEB scheme to calculate the diffusion barriers for H_2, CO_2 and CO. The starting and the end position of the molecular diffusion pathway are placed above and below the central pore while a linear interpolation between those points is used as an initial guess of the diffusion path. The energy maximum corresponds to the H_2 molecule sitting in the middle of the pore, with two H atoms distributing on both sides of 2D porous C_2N sheet. Similar configurations have also been found for CO and CO_2 passing through the pore of 2D porous C_2N sheet. The energy barrier of H_2 passing though 2D porous C_2N sheet was computed to be 0.18 eV, as shown in Fig. 2. It indicates H_2 can pass though 2D porous C_2N sheet easily under experimental conditions. The barrier for H_2 diffusion is much smaller than those for polyphenylene[12,13] and some of porous graphene structures[14, 15]. But for CO_2 and CO, they are much more difficult to pass though 2D porous C_2N sheet, for the calculated diffusion barriers are about 0.72 and 1.05 eV, respectively, much higher than that of H_2 (Fig. 2). These results are consistent with the fact that the width of the pore (3.0 Å) is in-between with the kinetic radius of H_2 (2.89 Å)[17] and those of CO_2 (3.30 Å) and CO and (3.76 Å)[18].

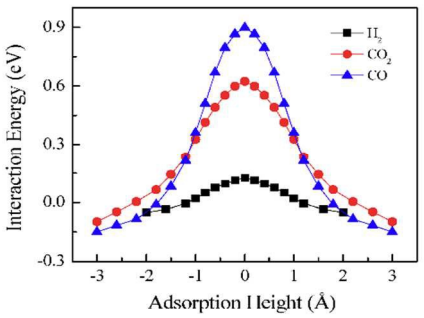

Figure 2 Interaction energy between H_2, CO_2, CO molecules and the 2D porous C_2N sheet as a function of adsorption height.

To quantitatively describe the hydrogen purification behaviour, the selectivity of 2D porous C_2N sheet for H_2 molecule over CO_2 and CO molecules can be estimated based on the computed diffusion barriers, according to the Arrhenius equation:

$$S_{H_2/gas} = \frac{D_{H_2}}{D_{gas}} = \frac{A_{H_2}}{A_{gas}} \frac{e^{-E_{H_2}/RT}}{e^{-E_{gas}/RT}}$$

where D is the diffusion rate, A is the diffusion prefactor, and E is the diffusion barrier. Here we assume that the prefactors of three gases are identical (A_{H_2}/A_{gas}= 1)[10], and the room temperature T is 300 K. 2D porous C_2N sheet exhibits obvious advantage for separating H_2 from CO_2 and CO, for the selectivity for H_2 over CO_2 and CO is quite high, 10^9 and 10^{14}, respectively. Compared with silica and carbon membranes[3, 17], which have the selectivity for H_2/CO and H_2/CO_2 in the order of 10 to 10^3, the selectivity of 2D porous C_2N sheet is remarkably high. Therefore, 2D porous C_2N sheet can be applied for efficient separation of H_2 from mixtures of large molecules.

We argue the origin of this high selectivity from both structural and electronic prospects of 2D porous C_2N sheet. The kinetic diameter of H_2 (2.89 Å)[20] is lower than the pore width of 2D porous C_2N sheet (3.0 Å). This explains why H_2 molecule can pass through the pore with a moderate 0.18 eV energy barrier. In contrast, the kinetic diameters for CO_2 and CO are 3.30 and 3.76 Å[21], respectively, which are much larger than the pore width of 2D porous C_2N sheet and hence make the diffusion of these molecules dynamically unfavourable. We can even speculate that the selectivity of 2D porous C_2N sheet for H_2/CH_4 should be also very high, due to the large kinetic radius of CH_4 (3.80Å)[20]. For a deeper understanding, we plotted the electron density isosurfaces for the molecules sitting in the middle of the pore at the same isovalue (0.05

e/Å^3) in Fig. 3. Obviously, H_2 almost has no electron overlap of the pore of 2D porous C_2N sheet, while CO has the most pronounced electron overlap, resulting the highest diffusion barrier. So, the selectivity is intrinsically due to the repulsive interaction between the molecules and 2D porous C_2N sheet.

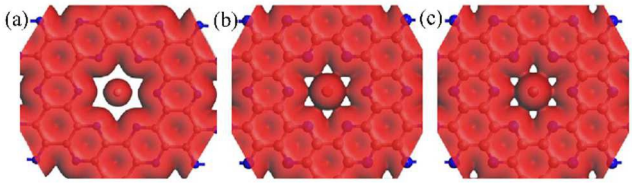

Figure 3 Electron-density isosurfaces for (a) H_2, (b) CO_2, and (c) CO sitting in the middle of the pore of 2D porous C_2N sheet. The isovalue is 0.05 e/Å^3.

The performance of a hydrogen purification membrane is not only determined by selectivity but also the permeance–flux. We performed the FPMD simulation to study the process of H_2 passing through the pores of 2D porous C_2N sheet, and estimate the H_2 flux. During a 6 ns run, we observed three H_2 molecules passing through porous C_2N sheet. Similar simulations for the CO_2 and CO molecules were performed, but no passing-through events were observed for the same time frame. So, the FPMD simulations further illustrate the high selectivity of 2D porous C_2N sheet for H_2/CO and H_2/CO_2 separation. Considering the number of passing through events (3) over the simulation time (6 ns) and taking into account the area of the membrane (240 Å^2), the flux of H_2 is about 0.0035 mol·cm^{-2}s^{-1}. Assuming a pressure drop of Δp = 1 bar across the pore, the H_2 permeance of 2D porous C_2N sheet is about 3.5×10^{-4} mol·m^{-2}·s^{-1}·Pa^{-1}, which is three orders magnitude less than that of porous graphene membrane reported by Jiang *et al.*[10] But is it still much larger than the industrially acceptable permeance for gas separation[29]. For example, a 30-nm-thick silica membrane has an H_2 permeance at an order of 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} at 673 K. Polymeric membranes usually have even lower H_2 permeance than oxide-based membranes. The high permeance of 2D porous C_2N sheet could be attributed to its one-atom thickness, as the permeance of a membrane is inversely proportional to its thickness.

Conclusions

In summary, one-atom thin porous C_2N sheet exhibits remarkably good performance in the H_2 selective permeation. The determined selectivity for hydrogen range from 10^9 up to 10^{14} over CO_2 and CO at room temperature with a H_2 permeance larger than 10^{-4} mol·m^{-2}·s^{-1}·Pa^{-1} and are superior to those of classical membranes. Since this well-defined one-atom thin porous C_2N sheet has recently been successfully synthesized, the proposed concept will hopefully inspire experimentalists for realizations of the superior H_2 purification membrane based on 2D porous C_2N sheet, which is a vital step for the realization of a clean energy economy.

This work was supported by the Fundamental Research Funds for the Central Universities, a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). We are grateful for the support of NSFC (11204123). The calculations were performed on parallel computers at the High Performance Computing Center (HPCC) of Nanjing University.

Notes and references

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