Two-dimensional polyphenylene: experimentally available porous graphene as a hydrogen purification membrane†

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We demonstrate computationally that two-dimensional polyphenylene is a typical semiconductor with a wide band gap, and the porous structure endows polyphenylene remarkably high selectivity for H_2 permeability relative to CO_2, CO and CH_4. This experimentally available porous graphene is expected to find applications in a hydrogen energy society.

Hydrocarbons, the organic compounds consisting entirely of hydrogen and carbon atoms, are one of the most important energy resources on earth and occur mainly in the form of crude oil and natural gas. Most hydrocarbons are linear chains, rings, or combinations of both. Inspired by the intensive studies of graphene,[1–10] Sofo *et al.*[11] proposed that, by adding a hydrogen atom to each carbon atom of graphene, the two-dimensional (2D) infinite hydrocarbon with the formula of C_nH_n, graphane, is thermodynamically stable and can form experimentally. They also predicted that graphane has a wide band gap, which was confirmed in following theoretical[12,13] and experimental studies.[14] However, in graphane, carbon and hydrogen atoms are not in the same plane, and carbon atoms have been converted from sp^2 to sp^3 hybridization which makes the carbon backbone non-planar. Therefore, an interesting question arises: could the sp^2-hybridized 2D infinite hydrocarbon exist? The answer is *yes*. Recently, by coupling well designed molecular building blocks (macrocycle cyclohexa-*m*-phenylene) on the Ag surface, Bieri *et al.*[15] have successfully fabricated regular 2D polyphenylene networks with single atom wide pores and sub nanometre periodicity, which is the first example of an sp^2-bonded hydrocarbon super-honeycomb network. More recently, similar porous polyphenylene frameworks have also been obtained by Chen *et al.*[16] From the structural viewpoint, 2D polyphenylene resembles graphene with periodically missing phenyl rings; thus it can be seen as porous graphene, which may show electronic properties and potential applications distinct from pristine graphene.

Moreover, due to the novel structural properties, 2D polyphenylene may find application in many fields such as a membrane for H_2 purification. H_2 production through the common method of steam–methane reforming[17] usually generates some less desirable species, including CO_2, CO and CH_4. Thus, separating H_2 from these species is of particular importance for its storage and usage.[18] Among the various strategies for H_2 separation, membranes have the advantages of easy operation, low energy consumption, and effective cost.[19] Many kinds of membranes have been developed for this target, such as metallic, silica, zeolite, carbon-based and polymer membranes.[20] The thickness of these membranes is usually in the range of 10–10^3 nm. Oyama *et al.*[21] proposed that the permeance of a membrane is inversely proportional to its thickness. Therefore, graphene, which is only one-atom thick, has once been considered as a promising membrane for gas separation. However, due to the densely packed honeycomb crystal lattice, perfect graphene membrane is impermeable even to gas molecules as small as helium.[22] To conquer this problem, hypothetical pores have been introduced into graphene sheets.[23,24] In a recent theoretical study, Jiang *et al.* demonstrated that by removing two neighboring rings from a graphene sheet, the resulting porous graphene can exhibit a high H_2 permeance relative to CH_4.[24] However, the precise realization of this kind of pore in graphene is rather challenging, and wider pores would let both gases pass without a barrier, which hence decreases the selectivity. In contrast, the pores in 2D polyphenylene are natural and uniformly distributed with the same width. Could 2D polyphenylene thus serve as a membrane for H_2 purification? In this work, density functional theory (DFT) computations were performed to address the above concerns.

Fig. 1a presents the optimized structure of a 2D polyphenylene layer in a 2 × 2 supercell, which includes 48 carbon atoms and 24 hydrogen atoms. Compared with graphene, whose unit cell contains two carbon atoms, the unit cell of 2D polyphenylene is composed of two C_6H_3 rings, which are linked by a C–C bond. The optimized lattice parameter for 2D

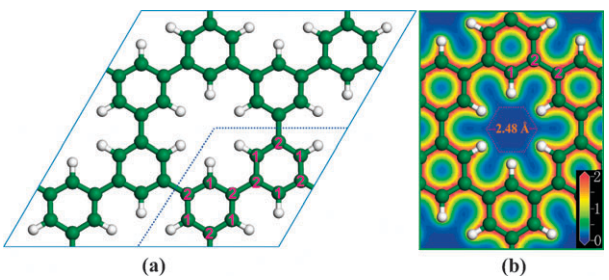

Fig. 1 (a) Top view of 2D polyphenylene layer in a 2 × 2 supercell. The dashed lines indicate a unit cell. Carbon and hydrogen atoms are denoted with green and white balls, respectively. Labels "1" and "2" represent the different carbon sites. (b) Total electron density projected on the surface of polyphenylene layer.

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polyphenylene is $a = b = 7.455$ Å (which is also the distance between two pores), and agrees well with the experimental value (7.4 Å).[15] There are two different carbon sites in a polyphenylene layer: C_1 atoms which bond to two carbon atoms and one hydrogen atom, and C_2 atoms which bond to three carbon atoms. As a result, two different types of carbon bonds are present: those connecting C_1 and C_2 atoms with a bond length of 1.40 Å and those connecting C_2 atoms with a bond length of 1.48 Å. The C_1–H bond length is 1.08 Å. The C_1–C_2 and C_1–H bond lengths are almost identical to the corresponding values in a free benzene molecule. Moreover, we plotted the projected electron density of a polyphenylene layer in Fig. 1b. Obviously the electron overlap between C_2–C_2 bonds are less pronounced than C_1–C_2 bonds. The pores of 2D polyphenylene show electron-deficient character. Also, we can see that the pore is hexagonal in shape and the width of pore is estimated to be ~2.48 Å.

On the basis of the optimized geometric structure, we computed the band structure and density of states (DOS) of 2D polyphenylene (Fig. 2a). A direct gap of about 2.48 eV appears for polyphenylene networks, with the valence band maximum (VBM) and conduction band minimum (CBM) both located at the K point. Therefore, different from graphene which is a semimetal with a zero band gap, 2D polyphenylene exhibits semiconducting characteristics, which is associated intrinsically with the existence of pores. Our result is also in good agreement with that of a recent computational study at the same theoretical level.[25] However, note that DFT usually underestimates band gaps, and the accurate computation of band gaps requires a quasiparticle approach. The partial DOS analysis shows that both C_1 and C_2 atoms contribute to the VBM and CBM, and the contribution from C_1 is more pronounced than that from C_2 atoms. To gain a deeper insight, we also computed the electron density isosurfaces for both VBM and CBM. As shown in Fig. 2b and c, the VBM of polyphenylene is mainly contributed by the p_z atomic orbitals of C_1 atoms and the sp^2 orbitals of C_1–C_2 bonds, and the CBM originates mainly from the p_z atomic orbitals of C_1 atoms and the sp^2 orbitals of C_2–C_2 bonds. Therefore, both VBM and CBM consist to some extent of π-type bonding states.

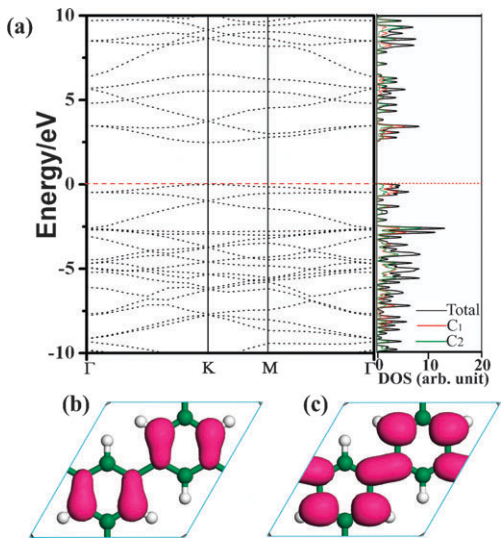

Fig. 2 (a) Electronic band structure (left) and density of states (DOS, right) of polyphenylene. The DOS is projected on C_1 (red) and C_2 (green) atoms. (b) and (c) are electronic profiles for VBM and CBM, respectively. The isovalue is 0.05 e Å^{-3}. The Fermi level is assigned at 0 eV.

Next we explored the capability of 2D polyphenylene for separating H_2 from several gas molecules, including CH_4, CO_2 and CO (C_n). The energy barrier for H_2 passing though the pore of polyphenylene was firstly computed. We examined several configurations for H_2 adsorption on top of the pore. The most stable configuration is that the axis of H_2 is perpendicular to the surface of polyphenylene. The adsorption energy is −0.03 eV, indicating a weak van der Waals (vdW) interaction. This configuration is set as the initial state (IS), and the configuration of H_2 adsorption on the opposite side of the pore is set as the final state (FS). The energy barrier was computed to be 0.61 eV (Fig. 3). This moderate energy barrier can easily be overcome by H_2 under experimental conditions. Similarly, the diffusion barriers for CH_4, CO_2 and CO passing though the pore were also computed, and the obtained values (2.21, 2.35 and 5.19 eV for CO_2, CO and CH_4, respectively) indicate that it is much more difficult for these molecules to pass though the pores of polyphenylene under normal experimental conditions.

On the basis of the computed energy barriers, we can estimate the selectivity of polyphenylene for the diffusion of H_2 relative to CH_4, CO and CO_2 (C_n) quantitatively according to the Arrhenius equation:

$$S_{H_2/C_n} = \frac{r_{H_2}}{r_{C_n}} = \frac{A_{H_2}}{A_{C_n}} \frac{e^{-E_{H_2}/RT}}{e^{-E_{C_n}/RT}}$$

where r is the diffusion rate, A is the interaction (diffusion) prefactor, and E is the diffusion barrier. Here we assume that the prefactors of four gases are identical ($A_{H_2}/A_{C_n} = 1$), and the room temperature T is 300 K. Thus we yield a selectivity of about 10^{26}, 10^{29} and 10^{76} for H_2/CO_2, H_2/CO and H_2/CH_4, respectively. Compared with silica and carbon membranes,[26,27] which have the selectivity for H_2/CH_4 and H_2/CO_2 in the order of 10 to 10^3, the selectivity of polyphenylene is remarkably high. Polyphenylene layer can actually block all molecules larger than H_2.

Finally, we argue the origin of this high selectivity from both structural and electronic prospects. As mentioned above,

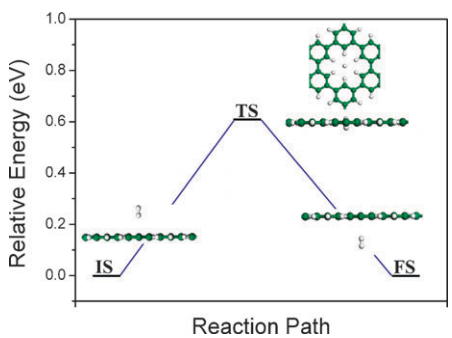

Fig. 3 Energy profiles for H_2 passing through the pore of polyphenylene. The insets are the corresponding configurations of IS, TS and FS. For the TS both top and side views are given.

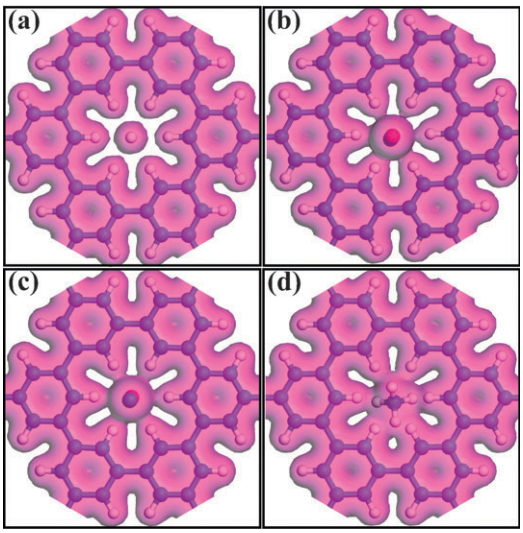

Fig. 4 Electron-density isosurfaces for (a) H_2, (b) CO_2, (c) CO and (d) CH_4 passing through the pore of polyphenylene at the transition states. The isovalue is 0.15 a.u.

the pore width of 2D polyphenylene is about 2.48 Å, which is lower than the kinetic diameter of H_2 (2.89 Å).[26] This explains why H_2 molecule can not pass through the pore freely and a moderate 0.61 eV energy barrier must be overcome. Jiang *et al.*[24] demonstrated that the barrier can decrease to zero if the pore is wider than 3.80 Å. In contrast, the kinetic diameters for CO_2, CO and CH_4 are 3.30, 3.76 and 3.80 Å, respectively, which are much larger than the pore width of polyphenylene and hence make the diffusion of these molecules dynamically unfavorable. Note that the barriers are consistent with their kinetic diameters relative to the width of pore. Therefore, the remarkably high selectivity of polyphenylene towards the above molecules is mainly determined by the pore width. For a deeper understanding, we plotted the electron density isosurfaces for the transition states (TS) of these four molecules at the same isovalue (Fig. 4). The electron overlap between H_2 and the pore of polyphenylene at TS is less pronounced than those of CO_2, CO and CH_4. Obviously, CH_4 has the most pronounced electron overlap with polyphenylene at TS, resulting in the highest diffusion barrier. Therefore, intrinsically it is the electron densities at the pores that repel these molecules to pass through the pores.

In summary, the structural and electronic properties of two-dimensional polyphenylene have been investigated *via* density functional theory computations. The structure of polyphenylene resembles graphene with periodically "missing" phenyl rings. Pristine polyphenylene is a semiconductor with a 2.48 eV direct band gap. The capability of polyphenylene for separating H_2 from several gas molecules, including CH_4, CO_2 and CO, was explored. Since the kinetic diameter of H_2 approaches the width of the pore of polyphenylene, H_2 can pass though the pore with a moderate barrier. However, the kinetic diameters of CO_2, CO and CH_4 are much larger than the pore width; therefore, the diffusion of these molecules is difficult. Polyphenylene thus exhibits remarkably high selectivity for H_2 separation from CO_2, CO and CH_4, and can serve as a superior membrane over traditional ones for H_2 purification, which is a vital technology for the realization of a hydrogen energy society.

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