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Nonzero Gap Two-Dimensional Carbon Allotrope from Porous Graphene

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Supporting Information

ABSTRACT: Graphene is considered one of the most promising materials for future electronics. However, in its pristine form, graphene is a gapless material, which imposes limitations to its use in some electronic applications. To solve this problem, many approaches have been tried, such as physical and chemical functionalizations. These processes compromise some of the desirable graphene properties. In this work, based on ab initio quantum molecular dynamics, we showed that a two-dimensional carbon allotrope, named biphenylene carbon (BPC), can be obtained from selective



dehydrogenation of porous graphene. BPC presents a nonzero bandgap and well-delocalized frontier orbitals. Synthetic routes to BPC are also addressed.

INTRODUCTION

In the last decades, the successive discoveries of new carbonbased materials have opened a new era in materials science. Examples of these discoveries are fullerenes,¹ carbon nanotubes,² and, more recently, graphene.^{3,4}

Graphene is a two-dimensional array of hexagonal units of sp² bonded carbon atoms (Figure 1a). Graphene presents very unusual and interesting electronic and mechanical properties.^{3,4} Because of these special properties, graphene is considered one of the most promising materials for future electronics. However, in its pristine form, graphene is a gapless semiconductor, as shown in Figure 2a. This poses serious limitations to its use in some electronic applications, such as some kinds of transistors.5

Many approaches have been tried to create a gap in graphene-like materials. The most common strategies use chemical and physical methods, such as oxidation,^{δ} hydrogenation,⁷⁻¹⁰ and fluorination.¹¹⁻¹³ However, the controlled synthesis of large structures and/or at large scale has been proved to be difficult. More important, the desirable electronic graphene properties are partially compromised in such approaches.

Another approach has been trying to obtain intrinsically hydrogenated structures, such as, the so-called porous graphene (PG) (Figure 1b),^{14–18} whose synthesis has been recently achieved.¹⁴ But again, the obtained structures present some of the same problems of chemically/physically functionalized graphene, such as excessive large bandgap value and flat (low mobility) electronic bands (Figure 2b).

An ideal structure would be an allotrope carbon form with an intrinsic good bandgap value and electronic bands with good dispersion (electron delocalization and high charge mobility). In theory, structures satisfying these conditions do exist, as the so-called biphenylene carbon (BPC) (Figures 1c and 2c).^{19,20} Molecular fragments in linear, zigzag, and several other forms have already been synthesized.²¹ They are considered as potential precursors for fullerenes, bowls, cyclophanes, etc.^{19–21} However, the synthesis of large BPC fragments remains elusive.

In this work, based on ab initio molecular dynamics simulations, we show that selective dehydrogenation of porous graphene leads to the spontaneous interconversion to BPC structures. Possible synthetic route approaches to achieve this interconversion are also discussed. That this interconversion was possible was found out by exploratory investigations, as discussed below.

METHODOLOGY

The geometric and electronic aspects of the structures shown in Figure 1, as well as the interconversion processes from PG to BPC, were investigated in the framework of density functional theory (DFT). Exchange and correlation terms were considered within the generalized gradient approximation (GGA) with a BLYP functional,²² with a double numerical plus polarization basis set, as implemented in DMol³ code.^{23,24} In all the calculations, a nonrelativistic and all-electron treatment was used. The parameter criteria for the tolerances of energy, force, displacement, and SCF convergence criteria were 2.72×10^{-4} eV, 5.44 \times 10⁻² eV·Å⁻¹, 5.0 \times 10⁻³ Å, and 1.0 \times 10⁻⁶, respectively.

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Figure 1. Structural models considered in the present work. (a) Graphene, with two atoms in the unit cell, (b) porous graphene with 18 atoms in the unit cell, and (c) biphenylene carbon (BPC) with 12 atoms in the unit cell. Unit cell is highlighted in each case.

It is well-known that although DFT methods can reliably describe the geometrical features in general some electronic properties, as the bandgap values, are underestimated.²⁵ For these reasons, for the analysis of the electronic band structure calculations, we used a DFT-based tight-binding method (DFTB+),^{26,27} which has been proved to reliably describe the electronic properties of carbon-based materials. The DFTB+ calculations were carried out using the optimized geometries from the DMol³ calculations. The DFTB+ nondiagonal matrix (overlap matrix and Hamilton matrix) elements are calculated in a two-center approximation. They are distant dependent and considered up to about 10 atomic units.

Initially, we carried out DMol³ fully (unit cell parameters and atomic positions were allowed to vary) geometric optimizations. The most relevant geometrical data are displayed in Tables 1 and 2. See also Supporting Information.

RESULTS

Our results show that the PG-optimized geometry is characterized by a $C222(D_2^6)$ symmetry group. The hexagonal geometry is preserved, with bond length in the rings and intrarings of 1.40 and 1.50 Å, respectively. The obtained



Figure 2. Band structure (in eV) for the (a) graphene, (b) porous graphene, and (c) BPC. Dashed red lines indicate the Fermi level. Please notice that DFTB+ convention to locate the Fermi level is at the value of the highest occupied state.

Table 1. DMol³ Geometrical Data^{*a*}

graphene				
distances (Å)		angles (deg)		
$C_1 - C_2$	1.39	$C_1 - C_2 - C_3$	119.96	
porous graphene				
distances (Å)		angles (deg)		
$C_1 - C_2$	1.41	$C_1 - C_5 - C_6$	121.56	
$C_3 - C_4$	1.41	$C_2 - C_1 - C_5$	122.68	
$C_{5}-C_{6}$	1.50	$C_1 - C_2 - C_3$	117.77	
BPC				
distances (Å)		angles (deg)		
$C_1 - C_2$	1.476	$C_1 - C_2 - C_3$	89.826	
$C_1 - C_4$	1.485	$C_2 - C_3 - C_4$	90.174	
$C_1 - C_5$	1.365	$C_2 - C_1 - C_5$	119.846	
^a Labels according to Figure 1.				

geometry is in good agreement with the experimental data reported, 14 and theory and experiment estimate the lattice parameter to be about 7.4 Å. The obtained bandgap value of 3.3

Table 2. Lattice Parameters for Graphene, Porous Graphene, and Biphenylene Carbon (BPC), Respectively

	a (Å)	b (Å)
graphene	2.40	2.40
porous graphene	7.52	7.53
BPC	6.78	6.69



Figure 3. DFTB+ frontier orbitals for hydrogenated and dehydrogenated porous graphene. (a) and (b) HOCO and LUCO for porous graphene. (c) and (d) HOCO and LUCO for dehydrogenated porous graphene.

eV is also in good agreement with previous theoretical calculations (3.2 eV).¹⁶

For the BPC layer, a stable conformation was obtained, satisfying the topological conditions of the theoretically proposed structures.^{19,20} In relation to PG, there is a significant lattice parameter contraction, from 7.5 to 6.8 Å, respectively (Table 2). The bond lengths in the hexagons preserve the pattern of alternating double and single bonds (1.48 and 1.36 Å, respectively), while the square structure (cyclobutadiene) is almost a perfect square (1.48 Å) (see Figure 1 and Table 1).

In Figure 2, we present the band structure results obtained from DFTB+ calculations. As expected, graphene presents a zero bandgap value, while PG and BPC have values of 3.3 and 0.8 eV, respectively. However, bandgap values and good dispersion of the frontier bands are not warranty of good conductors. Besides these aspects, another important characteristic which plays an important role in defining the electronic (conductivity) mobility of the material is the degree of electronic delocalization of the frontier crystalline orbitals. The electronic analyses we carried out here for ideal BPC structures are for neutral forms (no free carriers). To create these carriers is necessary, as usual, to dope the material. In ref 16, the doping of porous graphene has been addressed. The same principles can be used to dope BPC structures.

In Figure 3, we present the frontier orbitals HOCO (highest occupied crystalline orbital) and LUCO (lowest unoccupied crystalline orbital) for PG and BPC. As we can see from Figure 3, BPC presents more delocalized orbitals than PG. Particularly interesting is the BPC HOCO, which is well delocalized over the whole network, suggestive of a good conductor structure.



Figure 4. DMol³ molecular dynamics snapshots and total energy values as a function of time. (a) Completely dehydrogenated porous graphene on the initial stage. The highlighted carbons in red lead to the formation of a cyclobutadiene. (b) and (c) Intermediate stages. Notice that adjacent rings rotate in opposite directions. (d) Final stage after a complete rotation of 30° in each ring. (e) Time evolution for the total energy during the QMD simulation. Letter labels represent the energy of each snapshot.

Thus, in principle, BPC presents itself as an ideal structure for many electronic applications: good intrinsic bandgap value, bands with good dispersion, and delocalized frontier orbitals. Also, we calculated the values of the effective masses $(m^*/m_e = 0.26 \text{ and } m^*/m_h = 0.33$, for the conduction and valence effective masses, respectively). These values are consistent with those expected of a good conductor. However, as mentioned before, the synthesis of large BPC fragments from using chemical methods remains elusive. Through exploratory investigations, we found out that selective hydrogen removal from PG leads to a spontaneous interconversion to BPC.

We have carried out ab initio quantum molecular dynamics (DMol³), NVT ensemble, at different temperatures: 0 (just geometric optimizations), 300, and 600 K. We started from the optimized PG geometry, and then we removed the hydrogen atoms and let the system freely evolve in time (lattice parameter values and atomic positions free to vary). For all the investigated cases, we observed a spontaneous intercon-

version from dehydrogenated PG to BPC. The obtained BPC structures are thermally stable (at least up to 600 K).

In Figure 4, we present results for the calculations carried out at 300 K. In Figures 4a–4d, we show snapshots from the molecular dynamics simulations at successive time steps. We can see that the dehydrogenated PG undergoes structural rearrangements, mainly ring rotations (about 30°) coupled to a lattice parameter reduction leading to the formation of a cyclobutadiene motif (highlighted atoms in Figures 4a–4d) and consequently to the BPC formation. The whole process can be better visualized in the video in the Supporting Information.

In Figure 4e, we present the total energy values as a function of time of simulation. As we can see, starting from dehydrogenated PG, the system continuously evolves to more stable configurations, reaching a well-defined minimum, which is associated with the BPC formation. These results can be explained in terms of the relative stability of graphene, PG, and PBC.

The total energy values per carbon atoms (in relation to graphene) of dehydrogenated PG and BPC are 1.26 and 0.63 eV, respectively. In this sense, the removal of hydrogens from PG inverts the stability order in relation to BPC, BPC being now 0.63 eV per carbon atom more stable. Due to the similar topology, the interconversion easily occurs since it requires only ring rotations and the creation of new bonds forming the cyclobutadiene motif. These results strongly support that BPC can be obtained from PG by just selective dehydrogenation.

PG-selective dehydrogenation is within our present-day synthesis capabilities. Recently, significant experimental advances have been produced in selective dehydrogenation of hydrocarbons.^{28–31} Fullerenes,²⁸ nanographene flakes,²⁹ and even two-dimensional networks^{30,31} similar to BPC have already been achieved. See more details in the Supporting Information. Obtaining BPC from DPG using these techniques is perfectly feasible. We hope the present results will stimulate further works along these lines.

ASSOCIATED CONTENT

S Supporting Information

Brief discussion about simulations and MD videos. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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