

Modeling of Nontraditional Structures of Carbon

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The present contribution deals with one of the possible structure types of nongraphitic carbon adsorbents. The proposed structure consists of infinite strips of condensed aromatic rings arranged into a hexagonal honeycomb-like structure with the edge formed only by sp^2 carbon atoms. Quantum chemical calculations were performed at the UHF/STO-3G level using the CRYSTAL95 program package for periodical approach. The extremely high adsorption ability of some low-density paramagnetic carbon forms can be elucidated by the presence of the sp^2 honeycomb carbon structure and the specific properties of its electronic structure.

1. INTRODUCTION

Adsorption of gases on carbon-based adsorbents is a subject of growing interest of both experimental and theoretical investigations. Recent experimental studies include gas adsorption on activated carbon, carbon nanotubes,¹ and graphitic nanofibers.² Recent theoretical studies include simulations of N_2 and Br_2 adsorption in carbon nanotubes³ and simulations of hydrogen adsorption on graphite nanofibers,⁴ in carbon nanotubes,^{5,6} and in idealized carbon slit pores.⁶ A very strong motivation for studies of this mentioned type is the extreme industrial importance of carbon adsorbents for various gases. Despite a significant effort made in this area, some important details are still unknown. According to Wang and Johnson,⁶ no reasonable carbon-gas potential applied to the graphitic structures is able to elucidate the extremely high gas adsorption on some adsorbents, found by Chambers et al.² This is a challenge for theoreticians to find carbon structures that are able to mediate extremely high adsorption of gases.

A growing knowledge on various structures of elementary carbon is beneficial to studies in this area. A brief overview of known carbon allotropes (both existing and theoretically predicted) were provided by Heimann et al.⁷ In addition to two basic carbon allotropes, diamond and graphite, many forms of other carbon types exist. These additional forms can be divided into two principal groups.⁷ The first one comprises mixed short-range order carbon forms of more or less randomly arranged carbon atoms: various ill-defined carbon materials such as amorphous carbon, diamond-like carbon, and vitreous carbon as well as various carbon blacks, soot, cokes, etc. Heimann et al.⁷ assign to the first group of "mixed" form of carbon several hypothetical structures such as polycyclic 3D-carbon networks^{8–12} (including metallic carbon),⁹ superdiamond,^{13,14} and layer-chain carbons.^{15,16} A new class of pyrolytic carbon materials was prepared by chemical vapor infiltration of microporous zeolite powder

followed by removal of the zeolitic substrate.¹⁷ The second group includes carbon forms for which the hybridization of a carbon atom can be expressed as sp^n , where n can be a nonintegral but a fractional number.⁷ This group contains such interesting carbon structures such as fullerenes, carbon onions,^{18,19} and nanotubes^{20–22} and acetylenic allotropes of carbon containing alternating triple and single bonds.²³ Various diamond-graphite hybrid structures²⁴ and some polycyclic carbon networks (with strained cycles in their structure)^{25–28} were also assigned to this group of intermediate carbon forms.⁷

To find suitable candidates of structures with extremal adsorption ability from this incredibly rich set of possibilities, one has to take into account two important factors: the availability of a large surface and the presence of a steric or electronic strain which will enhance the interaction ability of carbon atoms with the adsorbate. However, the structure must stabilize such strained localities to brake the chemical reactivity. According to these criteria, we propose 3D structures consisting of infinite strips of condensed aromatic rings as models for high-efficient adsorbents. The strips of condensed rings are arranged into a hexagonal honeycomb-structure (Figure 1). A new chemical quality originates in the area of edges connecting three strips: In the case of the edge formed only by sp^3 atoms, the structure possesses a steric stress resulting in higher interaction ability of the edge atoms. In the case of the edge formed only by sp^2 atoms, the structure can be either a polyradical stabilized sterically or a system of alternating σ -bonds formed by 2p orbitals of edge carbons, causing again considerable steric stress. Also in both of these subcases the interaction ability of the edge atoms will be considerably enhanced. The hypothetical structure with an sp^3 edge was described and quantum-chemically studied using periodic MNDO calculations by Karfunkel and Dressler,⁸ as a strainless molecular model of a fragment of this type of structure can serve 9,9'-bitriptycyl.²⁹ The honeycomb structure with pure sp^2 carbon atoms was proposed by van Vechten and Keszler³⁰ as a low-density "honey-comb graphite" phase which accounts for the low density of the glassy carbon and soot. The same authors

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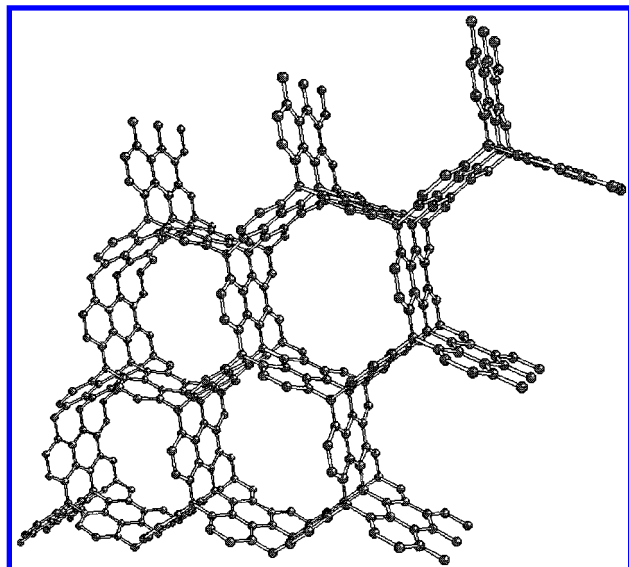


Figure 1. Three-dimensional periodic model of sp^2 honeycomb structure.

expected a significant ratio of this structure in very fine whiskers formed on the surface of graphite subjected to prolonged and moderately intense sputtering. Comparing experimental data with MNDO calculations, the authors³⁰ predicted in plasma, at conditions of the sputtering, the formation of a significant amount of 11-atomic carbon clusters tricyclo(3.3.3.0)^{1,5}undeca-2,7,9-triene-4,6,11-triyl (TUTT)³⁰ and tricyclo(3.3.3.0)^{1,5}undeca-2,7,9-triene (TUT). TUTT represents the basic building unit of the sp^2 edge of honeycomb carbon. Zerbetto³¹ obtained a very similar C_{14} cluster using the quantum Monte Carlo study based on EHT Hamiltonian. All these results encourage expectations that at least fragments of the structure shown in Figure 1 can exist in reality. This is a basis for our hypothesis that just such fragments are responsible for high adsorption capacity of some carbon adsorbents.

The electronic structure of a suitable one-dimensional periodic model that models the most important part of the honeycomb-like structure, namely, edge containing poly-radicals, is the subject of this study. The aim of the present paper is to study the character of the proposed carbon structure and its electron properties with the main emphasis on the estimation of the spin state of the unpaired electrons important for the interaction with the adsorbed gas.

2. MODELS AND COMPUTATIONAL DETAILS

A three-dimensional model (Figure 1) with elementary cells containing 14 carbon atoms (Figure 2) was used to compute the total energy of the structure of sp^2 honeycomb carbon and to calculate the unpaired spin populations. The geometry was constructed using the value of 0.143 nm for all C—C bond lengths (the C—C distance in graphite). For a more detailed study of the electronic structure of the edge with unpaired electrons in the 2p orbitals of carbon atoms, a one-dimensional model (1D-polymer) was used (Figure 3). The last model consists of three strips of condensed aromatic rings. The strips have one common edge, forming a trigonal star in the projection. The strips of aromatic rings are bonded together via sp^2 carbon atoms (edge atoms). The planes

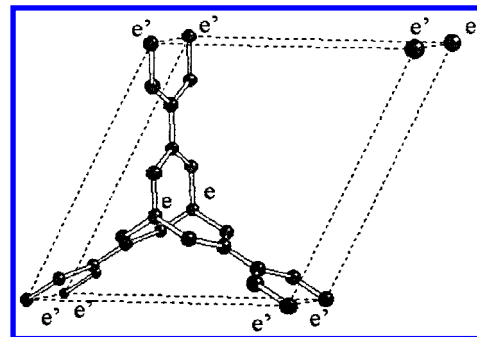


Figure 2. The unit cell of 3D-honeycomb carbon. The atoms denoted by e, e' are the edge carbons; all other atoms belong to aromatic rings. Note that each of the atoms marked by e belongs to two neighboring unit cells; thus the unit cell contains only one edge atom e' because each of the eight drawn atoms e' belongs to eight unit cells connected by a cell corner. The nearest neighboring atoms to e, e' atoms (12 totally) belong to two unit cells, so there are six atoms that belong to the unit cell considered. Finally, the unit cell contains six other carbon atoms which give a total of 12 nonedge carbon atoms and two edge atoms—a total of 14 carbon atoms in the unit cell.

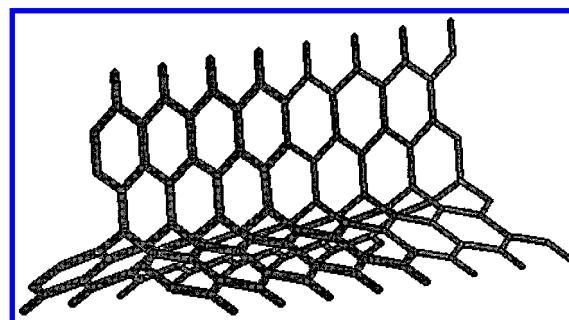


Figure 3. One-dimensional periodic model of sp^2 honeycomb structure.

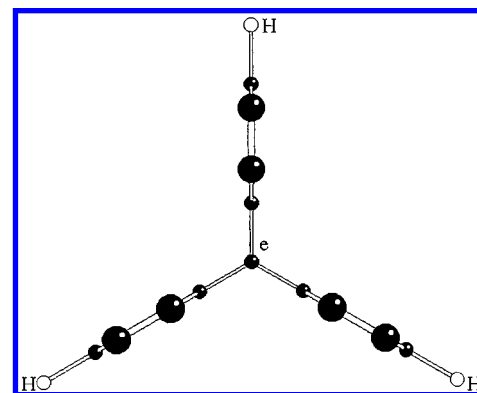


Figure 4. The unit cell of 1D model.

formed by σ -bonds of the edge atoms are perpendicular to the planes of all three strips. The remaining p-atomic orbitals of the edge atoms lie in the line of intersection of planes of the aromatic strips. The dangling bonds at the free sides of the aromatic strips are saturated by hydrogen atoms. The bond lengths for CH bonds were set to 0.108 nm. The elementary cell of this 1D model contains 13 carbon atoms and three hydrogen atoms (Figure 4). For the study of various possible spin states of this open-shell system, multiples of elementary cell were used.

Quantum-chemical calculations were performed using the periodic unrestricted Hartree–Fock method with STO-3G basis set (UHF/STO-3G) implemented in the CRYSTAL95 program package.³² Fixed geometry was used.

Table 1: Energies Per Elementary Cell (au) for a Different Number of Elementary Cells and Multiplicities

NEC\M ^a	1	2	3	4	5	6	8
1		488.083					
2	487.936		488.045				
3		488.138		488.101			
4	487.906		488.114		488.083		
5		488.142		488.118		488.094	
6	487.938		488.142		488.121		
7		488.140		488.125		488.109	488.091
8			488.129		488.114		

^a NEC = number of elementary cells, M = multiplicity.

3. RESULTS AND DISCUSSION

Periodical HF/STO-3G calculations were performed for both 3D models of honeycomb carbon and graphite to compare their stabilities. The computed total energy per one carbon atom is -37.421593 au for graphite and -37.399432 au for the 3D model of honeycomb carbon. Graphite is 0.022161 au (13.9 kcal/mol) more stable than honeycomb carbon. Because this difference is small enough, the existence of honeycomb carbon is quite possible.

Recalculation using 6-21G* basis set provides the total energy per one carbon atom -37.850505 au for graphite and -37.829973 au for honeycomb structure, respectively. In this basis set graphite is more stable by 12.9 kcal/mol than the honeycomb carbon. The effect of the basis set on the relative stability of the two carbon structures under consideration is indeed small. Note, that the difference of the total energies per one atom is identical with the difference of the heats of formation because the total energies of free atoms cancel in the terms subtracted.

The elementary cell of 3D model contains two "edge" atoms with unpaired electrons, giving rise to a triplet (ferromagnetic) state or a singlet (antiferromagnetic) state. The ferromagnetic state is the more stable one in this case. Using a doubled elementary cell that may provide singlet (antiferromagnetic), triplet (paramagnetic), and quintet (ferromagnetic) states, we obtained the triplet state as the most stable one. In both stable cases (triplet for single unit cell and triplet for doubled unit cell) the spin densities were localized on the edge carbons. The finding that the spin state changes with a change in the size of the elementary cell from the fully unpaired ferromagnetic state to the partially paired paramagnetic state shows that the symmetry of the electronic wave function is lower than the symmetry of the geometrical arrangement of atoms. This finding motivated us to investigate what multiplicity will be the most stable when the size of the elementary cell changes. Because the most interesting feature of the structure under the study is the edge which contains the polyradicals, the 1D models were used for the next study neglecting possible interactions of those radical centers separated by aromatic strips. In other words, we concentrated our interest on the direct spatial interaction of the edge radicals.

Table 1 contains the total energies per elementary cell computed for all multiples of the elementary cell ranging from one to eight elementary cells. The calculations were performed for all possible spin multiplicities of individual multiples; however, some of them did not reach convergency, e.g. antiferromagnetic state for octamer and ferromagnetic states for hexamer and octamer (all these are omitted in the

Table 1). The energies of the most stable spin states for individual multiples in Table 1 are emphasized with bold type. One can see that the most stable spin states are triplets for even-number elementary cells and doublets for the odd-number elementary cells. In all cases where a possibility other than ferromagnetic or antiferromagnetic state exists, i.e., a paramagnetic state, some paramagnetic states are the most stable ones. The expectation, according to the Hund's rule, is the maximum multiplicity (the ferromagnetic state). Our computation shows that the most stable spin state of the radical-containing edge does not follow this rule and that one of the possible paramagnetic states is the most stable one. However, the UHF method contains some spin contamination, namely, the admixture of some state with higher multiplicity to the actual one. The most significant admixture to the state with multiplicity M is from the state with multiplicity M+2.³³ If the behavior of the system studied was following Hund's rule (e.g. the state with maximum multiplicity was the most stable one), then no admixture of this state to some state with higher energy could change their ordering on the basis of energy. Moreover, the energy differences between individual states (around 0.02 au) are large enough to prevent the change of the energy ordering of states due to the artifact of the spin contamination. Therefore, despite of the fact that the UHF energies are not the exact energies of the pure spin states considered, the identification of the most stable state is correct. The lowest total energies are obtained for the doublet state of the pentamer (-488.142 au per elementary cell), triplet state of the hexamer (the same energy as in the previous case), and doublet of the heptamer (-488.140 au). The triplet state of the hexamer will be considered as the most suitable model of the linear polymer representing the edge of the structure of the honeycomb carbon. The reason is its energetic stability and the fact that the systems with an even number of radical centers can be in the ferromagnetic, antiferromagnetic, or paramagnetic state, in contrast to odd-numbered multiples of the elementary cell which cannot be antiferromagnetic. So the even-numbered multiple provides all possible spin states, and its most stable state seems to be the naturally occurring state of such a system. The paramagnetic triplet state of the model is consistent with the experimental findings that the fractional structures of carbon obtained by plasma sputtering or by synthesis in zeolites¹⁷ are paramagnetic. On the other hand, we cannot compare directly the experimental results with the theory, because the experimentally studied systems do not have a well described structure. However, one can say that the experimental data do not exclude the existence of the proposed structure. The spin densities are

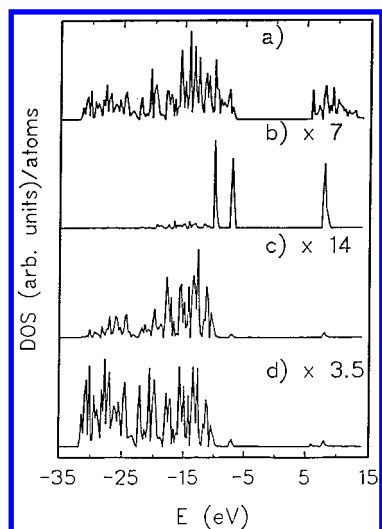


Figure 5. (a) Total DOS for the triplet state of the hexameric 1D model, (b) projected DOS of p_x orbitals of edge carbon atoms for hexameric model, (c) projected DOS of p_x orbitals of carbons neighboring with the edge carbons, and (d) projected DOS of $2p_x$ and $2s$ AOs of aromatic carbons.

localized on the edge atoms for all 1D models studied. Comparison of spin densities obtained for the 3D model (1.186) and for the triplet state of the hexameric 1D model (1.216) shows a small difference.

Figure 5a shows the density of states (DOS) for the triplet state of the hexameric 1D model. The total DOS shows the upper edge of the valence band at energy -6.5 eV, and the bottom edge of the conduction band is at $+5.6$ eV, giving the gap 12.1 eV. It is well-known that the Hartree–Fock method overestimates the excitation energies. Thus, the values obtained using this method are used for qualitative considerations only, not for quantitative conclusions based on the actual values of the width of the band gap. The first qualitative conclusion is that the 1D system is an insulator. The unpaired electrons are expected to be localized in the $2p_x$ orbitals of the edge atoms (x axis being the direction of axis of the 1D polymer). These atomic orbitals (AOs) are in mutual σ -position; the interatomic distance of the edge atoms is 0.245 nm. Formation of weak σ -bonds by these atomic orbitals is expected.

The projected DOS (PDOS) in Figure 5b shows two significant valence bands and one band in the conduction area formed by the p_x AOs of the edge carbon atoms. Therefore the PDOS showing bands originating from the $2p_x$ AOs of the edge carbons is of interest. The $2p_x$ AOs of atoms neighboring with the edge carbons could be capable of π -type interaction with the $2p_x$ AOs of the edge atoms; therefore, PDOS corresponding to the AOs is shown in Figure 5c. The π -system of the aromatic part of the structure is formed by appropriate contributions of $2p_y$ and $2p_z$ AOs of the aromatic carbons, while another combination of these AOs contributes in the σ -skeleton of the aromatic systems. On the other hand, $2p_x$ and $2s$ AOs of aromatic carbons are involved purely in the σ -bonds of aromatic skeleton. Therefore, the PDOS showing bands originating from the last AOs are used to identify the position of σ -bonds (Figure 5d).

A comparison of this PDOS (Figure 5b) with other ones (Figure 5c,d) shows that the interaction of the edge carbon p_x AOs with other AOs of the system is negligible. We

therefore ascribe the states coming from these AOs of the edge atoms with energy about -10 eV (Figure 5b) to weak σ -bonds between the edge atoms, while the band centered $+8$ eV corresponds to the σ^* -antibonding interaction. The top edge of the valence band of total DOS is formed by the $2p_x$ AOs of the edge atoms, containing the unpaired electrons. The σ -bonding and pure p bands formed by $2p_x$ AOs of edge atoms corresponds to the partial pairing of electrons in the polyradical edge and therefore to the nonmaximum multiplicity.

The conduction band in the total DOS is clearly divided into two subbands: subband under 7.5 eV and the part over 7.5 eV. As seen from the PDOS, the p_x AOs of the edge atoms contribute to the bottom part of the higher part of the conduction band. As shown in the previous discussion, the last is the σ^* -antibonding band, while the lower lying conduction band corresponds to π^* -antibonding orbitals of the aromatic strips. (Compare total DOS in Figure 5a and the σ -DOS in Figure 5d.)

If the obtained period of translational invariance of the electron wave function (the supercell of six unit cells) is correct, then the energies of spin multiplets of a system made of any multiple of this supercell can be described by a spin Hamiltonian of supercell-spin interactions, each supercell possessing a spin of the most stable multiplet for the supercell (e.g. $S = 1$ for triplet). Using the basis set of product spin functions one can construct the matrix of the spin Hamiltonian and the matrices of the operators \mathbf{S}^2 and \mathbf{S}_z as well.³⁴ These operators mutually commute, so one can find a set of eigenvectors common for $\{\mathbf{H}, \mathbf{S}^2, \mathbf{S}_z\}$ and to assign this way the eigenvalues of the spin Hamiltonian to the individual spin multiplets. To construct the spin Hamiltonian, the matrix of spin–spin interaction constants must be known. Considering only nearest-neighbor interactions, the matrix of spin–spin interaction constants will have the form of a tridiagonal matrix with a zero diagonal and all other nonzero elements equal to the value of the spin–spin interaction constant. Consideration of Born–von Karman periodic boundary conditions results only in a slight modification of the tridiagonal matrix—in addition, the upper most right and lower most left matrix elements will be nonzero, too. Thus, the energies of all spin multiplets of any multiple of the correct supercell will be described by only one value of spin–spin interaction constant between the neighboring supercells. The value of this interaction constant can be obtained from the differences of energies of individual multiplets of the doubled supercell, obtained via quantum-chemical calculation. A comparison of differences of multiplet energies computed quantum-chemically with those computed using spin-Hamiltonian for three or more supercells can serve as a test of correctness of the choice of the supercell. The test of correctness of the nearest-neighbor approximation can be performed as well, if one will take into account the interaction of the second, .. etc. neighboring supercells in completely analogical way. The improvement of accuracy of computations via the use of better basis sets is an unavoidable condition, however, far from being sufficient. To obtain the value of the spin–spin interaction constant of the neighboring supercells and the energies of individual multiplets with sufficient accuracy, at least the effect of spin-contamination should be removed and the effect of electron correlation should be taken into account

Table 2: Spin Densities on the Edge Carbons in Triplet and Hexamer

system edge carbon\M ^a	hexamer		trimer	
	3	5	2	4
C ₁	1.460	1.446	1.305	1.435
C ₂	1.460	1.312	-1.091	-1.088
C ₃	-0.932	-1.088	1.305	1.313
C ₄	1.460	1.448		
C ₅	1.460	1.460		
C ₆	-0.932	-0.933		

^a M = multiplicity.

at least at a simplified level. Unfortunately, the computational methods with inclusion of the spin projection and electron correlation are still yet not available for the calculations of periodic systems. However, as these improvements can be done for cluster (molecular) calculations, the periodic system can be approached by a cluster of suitable size (of course, properly embedded to conserve the properties of an extended system)³⁵ on a required methodological level. In this context, the present periodic Hartree–Fock UHF study can serve at least two purposes: the estimation of suitable candidates for the supercell and the calculation of electronic properties which have to be reproduced when using a cluster model in the sense described above. Cluster modeling using a multi-reference CI method accompanied with a test of the constancy of spin–spin interaction constant is the subject of forthcoming continuation of this work.

Table 2 shows the spin densities on the edge carbon atoms for hexamer (triplet), hexamer (quintet) and trimer (doublet), trimer (quartet). The hexamer (singlet) is omitted because of zero spin densities. The hexamer (heptet) is also omitted because for this system the convergency of SCF process was not reached. The spin density of hexamer (triplet) (the most stable multiplet of the hexamer) shows periodic behavior with the period of three atoms. In addition, the spin densities of the pairs C₁ and C₂ (or, equivalently, C₄ and C₅) are equal. A similar effect of “equal pairs” (C₁ and C₃) is observed for the trimer (doublet), while for the less stable trimer (quartet) this effect is missing. Based on these facts also the supercell made of three unit cells could be considered as a suitable candidate for the minimal supercell. Obviously, any multiple of the minimal supercell would be a correct supercell, too; however, finding the smallest supercell is highly desirable.

The partial unpairing of electrons of the edge polyradical enhances the interaction potential of this part of the structure, while the partial electron pairing brakes the chemical reactivity, so the intensity of the interaction with a potential adsorbate could be a strong physical (reversible) interaction but not a chemical (irreversible) one. Strong electron acceptor adsorbates can interact with the 2p_x AOs of the edge atoms, because the electrons in the corresponding valence band have the maximum energy. On the other hand, a potential adsorbate with strong electron donor properties can interact with the π^* -antibonding orbitals of the aromatic strips.

4. CONCLUSIONS

Considering that calculated total energies of graphite and sp² honeycomb carbon are comparable and that carbon samples with possible similar structures are paramagnetic the existence of the proposed honeycomb structure studied

may be concluded as possible. Localization of high spin density on the edge carbons for all models studied pre-determines higher interaction ability of this part of the structure with potential partners. On the other hand, the partial pairing of unpaired electrons lowers the chemical reactivity of the edge carbons which can lead to reversible, physical interactions with a potential adsorbate. Moreover, the interactions with an electron donor or acceptor can play a relatively important role. These facts support the hypothesis that a sp² honeycomb structure may be responsible for the high adsorption ability of some low-density paramagnetic carbon forms.

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Supporting Information Available: Honeycomb carbon, graphite, and output honeycomb carbon. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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